Viscosity Calculations for Ionic Liquid−Cosolvent Mixtures Based on Eyring's Absolute Rate Theory and Activity Coefficient Models

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The modeling of transport properties of nonaqueous mixtures containing ionic liquids (ILs), such as viscosities, is still in its infancy. The aim of this work is to evaluate the capability of viscosity models that are based on Eyring's absolute rate theory and activity coefficient models to nonaqueous mixtures containing ILs. The Eyring-NRTL (nonrandom two-liquid) and Eyring-UNIQUAC (universal quasichemical activity coefficient) equations were extended to modeling ILs with cosolvent mixtures. The results were compared and discussed. For systems with large nonideality the Eyring-NRTL equation needs three adjustable parameters to give satisfactory results, while the two-parameter Eyring-UNIQUAC model could give completely satisfactory results for these systems. Less adjustable parameters will be beneficial when limited experimental data are available. So, the Eyring-UNIQUAC equation was further simplified to have only one adjustable parameter by suitable assumptions.

Introduction

Low-melting organic salts or ionic liquids (ILs) have been vigorously investigated in the past decade. Because they are salts, they exhibit negligible vapor pressure and, therefore, cannot contribute to air pollution.[1] In addition, the physical properties are tunable by judicious selection of cation, anion, and substituent. So far, most efforts in researching ILs have been focused on the usefulness and application of ILs in various fields, such as new media for chemical synthesis,[2] separation science,[3] and biocatalysis[4] and as solvent-free electrolytes for electrochemical devices and processes,[5] while the thermodynamic modeling investigations of properties of ILs and in particular of mixtures containing ILs have lagged behind.[6]

The knowledge of thermodynamic properties and modeling of mixtures containing ILs are of considerable importance in the development of practical applications and design of processes as mentioned above. To date, a number of activity coefficient models have been studied for its ability to describe kinds of equilibrium properties of mixtures containing ILs. The vapor−liquid equilibrium (VLE) of systems containing ILs has been successfully described by nonrandom two-liquid (NRTL),[7,8] universal quasichemical activity coefficient (UNIQUAC),[7] universal functional activity coefficient (UNIFAC(Do)),[9] and conductor-like screening model for realistic solvents (COSMO-RS)[9,10] methods. The liquid−liquid equilibrium (LLE) have also been systematically studied through NRTL,[11,12] electrolyte-NRTL,[13] UNIQUAC,[13,14] and COSMO-RS[15] models. The descriptions of solid−liquid equilibrium (SLE) have been performed using the NRTL,[16] Wilson,[17] and UNIQUAC[17] models. Recently, Belvèze et al.[18] compared the electrolyte-NRTL equation and Pitzer model to the modeling of activity coefficients of aqueous solutions of quaternary ammonium salts. The successful applications of these molecular thermodynamic models to the equilibrium properties of IL systems including VLE, LLE, and SLE, and so forth, make it feasible to the simulation and optimization the processes involving IL−cosolvent mixtures. Besides the phase equilibrium properties, the flow properties of mixtures, such as the viscosities, also play an important role in chemical engineering process. At present, however, systematic studies of viscosity models for mixtures containing ILs are still rare.

In the chemical industry, information about the viscosity of liquid mixtures and their dependence on composition plays an important role in the design of heat transfer equipment, process piping, liquid−liquid extractors, and other units. Because of its importance, many papers have already been devoted to the experimental determination of viscosities of IL−cosolvent systems.[6] Since it is infeasible to experimentally determine the viscosity of IL−cosolvent systems for every imaginable composition and temperature, semitheoretical models that are fitted to a small number of available experimental data are more routinely applied in process simulation. Seddon et al.[19] systematically investigated the influence of cosolvents on the viscosity of ILs and found empirically a single exponential equation (Seddon equation) with only one fitting parameter. This equation is widely used and investigated its applicability to correlate viscosity of ILs with cosolvents.[20−23] On the other hand, a viscosity model based on Eyring's absolute rate theory and activity coefficient model has been successfully applied to correlate molecular−molecular[24−26] and molecular−polymer mixtures.[27,28] It is widely recognized that Eyring's absolute rate theory for viscosity has made a bridge between transport and thermodynamic properties. Models for liquid mixture viscosity originally developed under Erying's absolute reaction theory have been reviewed recently.[29] These results suggest that viscosity calculations may also be enhanced when applying Eyring's absolute rate theory with the activity coefficient model to IL−cosolvent mixtures.

It is, therefore, the purpose of this paper to investigate the applicability of Eyring's absolute rate theory with the activity

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coefficient model to describe viscosities of IL−cosolvent systems. The models tested in this work include the Eyring-UNIQUAC and Eyring-NRTL equation. The results show that better results can be obtained by the Eyring-UNIQUAC equation with two parameters. Furthermore, it may happen that experimental data for a given IL−cosolvent mixture are so fragmentary that it is not possible to determine two or three meaningful parameters. In that event, limited data can often yield only one significant binary parameter. So, the Eyring-UNIQUAC equation is then modified into the formulation with only one parameter. The results of the simplified Eyring-UNIQUAC equation are discussed and compared with the one-parameter Seddon equation. It can be found that the simplified Eyring-UNIQUAC equation can describe viscosities of IL−cosolvent systems satisfactorily.

Theory Background

According to Eyring's absolute reaction rate theory, viscous flow can be regarded as an activated process.[30] An activation energy Δg^{Θ} has to be exerted to move the sliding layer from one energy minimum to the next by one flow unit. The viscosity of any system can be expressed as

$$\eta = \frac{hN}{V}\exp\left(\frac{\Delta g^{\neq}}{RT}\right) \qquad (1)$$

In eq 1, η is shear viscosity, h is the Planck constant, N is the Avogadro's number, and V is the molar volume of the system.

In the case of an ideal binary system, the following mixing rule is defined.

$$\Delta g^{\neq} = x_1\Delta g_1^{\neq} + x_2\Delta g_2^{\neq} \qquad (2)$$

Combining this equation with eq 1 leads to an expression for the mixture viscosity of an ideal binary system.

$$\eta_{\text{mix}} = \frac{hN}{V_{\text{mix}}}\exp\left(\frac{x_1\Delta g_1^{\neq} + x_2\Delta g_2^{\neq}}{RT}\right) \qquad (3)$$

If eq 1 is also used to describe the pure component viscosity, including ILs, then eq 3 can be rewritten as

$$\ln(\eta_{\text{mix}}V_{\text{mix}}) = x_1\ln(\eta_1V_1) + x_2\ln(\eta_2V_2) \qquad (4)$$

However, this equation holds only in the case of thermodynamically ideal binary systems. The ILs can act both as a hydrogen-bond acceptor (anion) and donor (ion) and could be expected to interact with solvents which have both accepting and donating sites. So there is clearly hydrogen-bond interaction between the ILs and cosolvents. While for nonideal systems, the molar free energy of activation for the flow process can be regard as the sum of an ideal contribution and a correction or excess term. Therefore, eq 2 may be corrected as

$$\Delta g^{\neq} = \Delta g_{\text{ideal}}^{\neq} + g_{\text{E}}^{\neq} = x_1\Delta g_1^{\neq} + x_2\Delta g_2^{\neq} + g_{\text{E}}^{\neq} \qquad (5)$$

where $\Delta g_{\text{ideal}}^{\Theta}$ is the ideal mixture contribution and g_{E}^{Θ} is the excess activation energy for the flow process.

Finally, the dynamic mixture viscosity is given by the following expression:

$$\ln(\eta_{\text{mix}}V_{\text{mix}}) = x_1\ln(\eta_1V_1) + x_2\ln(\eta_2V_2) + \frac{g_{\text{E}}^{\neq}}{RT} \qquad (6)$$

As stated previously by Eyring[30] and other authors,[24−29] there is a close analogy between the excess activation energy for the flow process and the respective excess free energy of mixing. Therefore, it is reasonable to correlate the g_{E}^{Θ}/RT term in eq 6 with the thermodynamic parameters characteristic of the interaction between components. In other word, the nonideal part, g_{E}^{Θ}/RT, could function by any form of the excess Gibbs free energy function.

In this study two methods, namely, the Eyring-NRTL[27] and Eyring-UNIQUAC[24,25] models, are used to correlate the viscosity of nonaqueous mixtures containing ILs. These two models make use of the NRTL and UNIQUAC equations to represent the nonideal part, g_{E}^{Θ}/RT, in eq 6, respectively.

(1) The correlative Eyring-NRTL equation was originally developed by Novak[27] for calculating viscosities of polymer−solvent systems. In the Eyring-NRTL equation, g_{E}^{Θ}/RT is correlated with:

$$\frac{g_{\text{E}}^{\neq}}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_2G_{21} + x_1} + \frac{\tau_{12}G_{12}}{x_1G_{12} + x_2}\right) \qquad (7)$$

with $\ln G_{12} = -\alpha\tau_{12}$ and $\ln G_{21} = -\alpha\tau_{21}$ for which

$$\tau_{ij} = (g_{ij} - g_{ji})/RT = \Delta g_{ij}/RT \qquad (8)$$

Here, the parameter g_{ij} characterizes the interaction between substances i and j, while the parameter α is related to the nonrandomness in the mixture (when $\alpha = 0$ represents an ideal solution, or complete randomness).

The Eyring-NRTL equation for binary systems is then written as:

$$\ln(\eta_{\text{mix}}V_{\text{mix}}) = x_1\ln(\eta_1V_1) + x_2\ln(\eta_2V_2) + x_1x_2\left[\frac{\tau_{21}\exp(-\alpha\tau_{21})}{x_1 + x_2\exp(-\alpha\tau_{21})} + \frac{\tau_{12}\exp(-\alpha\tau_{12})}{x_2 + x_1\exp(-\alpha\tau_{12})}\right] \qquad (9)$$

with interaction parameters $g_{12}-g_{21}$ and $g_{21}-g_{11}$, which are given in eq 8. There are three parameters, α, Δg_{12}, and Δg_{21}, in the above Eyring-NRTL equation. Although α can be treated as an adjustable parameter, it is considered here to be fixed at 0.25 as a base case for immiscible binaries,[31] so that the Eyring-NRTL equation compared will have two adjustable parameters.

(2) The Eyring-UNIQUAC equation proposed by Martins et al.[24,25] for organic molecular mixtures uses the UNIQUAC model to describe the g_{E}^{Θ}/RT term and has the final form for binary mixtures as

$$\ln(\eta_{\text{mix}}V_{\text{mix}}) = x_1\ln(\eta_1V_1) + x_2\ln(\eta_2V_2) + x_1\ln\frac{\phi_1}{x_1} + x_2\ln\frac{\phi_2}{x_2} + 5\left(q_1x_1\ln\frac{\theta_1}{\phi_1} + q_2x_2\ln\frac{\theta_2}{\phi_2}\right) - x_1q_1\ln(\theta_1 + \theta_2\tau_{21}) - x_2q_2\ln(\theta_2 + \theta_1\tau_{12}) \qquad (10)$$

and

$$\tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) \tag{11}$$

here q_i is the surface area parameter, θ_i is the surface area fraction, ϕ_i is the volume fraction, and Δu_{ij} are the interaction parameters. The binary interaction parameters Δu_{ij} are estimated from experimental viscosity data. More details of the UNIQUAC model and the calculation of surface area fraction, θ_i, and the volume fraction, ϕ_i, are given elsewhere.[31]

The use of one system of parameters to correlate all of the data with different temperatures will facilitate the calculation of viscosity at certain temperatures that are not experimentally determined. When the viscosity data for IL−cosolvent mixtures are available at different temperatures, the interaction energy parameters in Eyring-NRTL and Eyring-UNIQUAC equations are taken as linear temperature dependence:

$$P(T) = P_a + P_b(T/\mathrm{K}) \tag{12}$$

where P_a and P_b are two adjustable parameters for each interaction energy parameter.

The adjustable parameters were found by an optimization technique using Marquardt's maximum likelihood method of minimization

$$F = \sum_{i=1}^{N}\left[\frac{\ln(\eta_{i,\mathrm{exp}}) - \ln(\eta_{i,\mathrm{cal}})}{\ln(\eta_{i,\mathrm{exp}})}\right]^2 \tag{13}$$

where F is the objective function, N is the number of experimental points, respectively, and $\eta_{i,\mathrm{exp}}$ and $\eta_{i,\mathrm{calc}}$ are the experimental and calculated dynamic viscosity, respectively.

Correlation Results and Discussion

A database of experimental viscosities of nonaqueous mixtures containing ILs available in the open literature was collected. A global number of 1504 data points for several ILs with differential organic compounds, covering wide ranges of viscosity, (0.4 to 21000) cP, were used in this study. The viscosities were determined by different methods, such as falling-ball viscometer, rotational viscometer, or Ubbelohde viscometer in the references. The uncertainty of the measurements can be found in the corresponding reference. Table 1 summarizes the fitting results according to the different classes of liquid mixtures. When the viscosity data for IL−cosolvent mixtures are available at different temperatures in Tables 1 and 2, the linear temperature dependence of parameters as shown in eq 12 is adapted. So, for these systems actually four adjustable parameters are obtained. The average absolute deviation (ADD) of dynamic viscosity is given by

$$\mathrm{ADD} = \frac{100\ \%}{N}\sum_{i=1}^{N}\frac{|\eta_{i,\mathrm{exp}} - \eta_{i,\mathrm{calc}}|}{\eta_{i,\mathrm{exp}}} \tag{14}$$

It can be seen that the Eyring-UNIQUAC models give a very good representation of viscosity data with small ADD's which is little better than the Eyring-NRTL equation. Viscosity may be a limiting factor for the industrial application of ILs if pumping costs become prohibitive. Of course, in many real systems the IL could be mixed with other liquid components, which would cause the viscosity of the mixture to be much lower. The Eyring-UNIQUAC model could facilitate the calculation of IL−cosolvent viscosity of these systems.

Table 1. Results of Different Equations for the Viscosity Calculation of Mixtures Containing ILs

mixture (1)−(2)	n_p	T(K)	ADD % Eyring-NRTL	 Eyring-UNIQUAC
[C$_4$mim]BF$_4$−DMF[21]	15	298.15	2.70	2.65
[C$_4$mim]BF$_4$−2-butanone[21]	15	298.15	1.68	1.83
[C$_4$mim]BF$_4$−acetonitrile[32,33]	28	298.15	1.29	1.31
[C$_4$mim]BF$_4$−dichloromethane[32,33]	15	298.15	5.43	3.52
[C$_4$mim]BF$_4$−ethanol[32,33]	13	298.15	2.26	3.41
[C$_8$mim]BF$_4$−dichloromethane[32,33]	15	298.15	12.38	4.40
[C$_8$mim]BF$_4$−2-butanone[32,33]	15	298.15	2.68	2.52
[C$_8$mim]BF$_4$−1-propanol[34]	15	298.15	0.86	0.65
[C$_8$mim]BF$_4$−2-propanol[34]	15	298.15	1.66	1.40
[C$_8$mim]BF$_4$−ethanol[34]	15	298.15	0.63	0.65
[C$_8$mim]BF$_4$−methanol[34]	15	298.15	8.14	2.09
[C$_4$mim]PF$_6$−2-butanone[35]	15	298.15	1.29	1.50
[C$_4$mim]PF$_6$−acetone[35]	15	298.15	0.87	0.99
[C$_4$mim]PF$_6$−cyclopentanone[35]	15	298.15	1.11	1.10
[C$_4$mim]PF$_6$−ethyl acetate[35]	15	298.15	2.54	3.00
[C$_4$mim]PF$_6$−pentanone[35]	15	298.15	1.61	2.15
[C$_4$mim]PF$_6$−DMSO[20]	15	298.15	1.93	2.03
[C$_4$mim]PF$_6$−acetonitrile[20]	15	298.15	3.06	3.03
[C$_4$mim]PF$_6$−methanol[20]	15	298.15	5.29	5.45
[C$_4$mim]PF$_6$−THF[20]	15	298.15	2.57	2.38
[C$_2$mim]EtSO$_4$−ethanol[36]	26	298.15	1.15	1.22
[MTEOA]MeSO$_4$−ethanol[37]	18	298.15	16.37	1.20
[C$_4$mpy]BF$_4$ + methanol[38]	39	298.15−323.15	0.93	0.96
[C$_4$mim]ClO−ethanol[39]	69	283.15−343.15	3.84	3.73
[C$_8$mim]BF$_4$−ethanol[39]	78	283.15−343.15	6.77	6.85
[C$_8$mim]Cl + 1-propanol[40]	39	298.15−328.15	3.90	3.86
[C$_8$mim]Cl + ethanol[40]	33	298.15−328.15	3.31	3.32
[C$_8$mim]Cl + methanol[40]	45	298.15−328.15	4.47	4.14
[C$_2$mim]EtSO$_4$−1-propanol[41]	33	298.15−328.15	1.23	1.25
[C$_2$mim]EtSO$_4$−2-propanol[41]	33	298.15−328.15	1.00	0.89
[C$_2$mim]EtSO$_4$−methanol[41]	39	298.15−328.15	8.54	5.93
[C$_4$mim]MeSO$_4$−ethanol[42]	39	298.15−328.15	1.54	1.72
[C$_2$mpy]EtSO$_4$ + ethanol[43]	36	298.15−328.15	3.33	3.11
[C$_4$mim]PF$_6$ + MEA[44]	88	288.15−323.15	3.49	3.94
[C$_2$mim]PF$_6$ + DMEA[44]	88	288.15−323.15	2.74	3.05
total	1014		3.50	2.61

The authors are aware of the fact that the Eyring's absolute theory and excess free energy models chosen do not account for ILs. The same-size billiard ball type model was used by Eyring and co-workers in the absolute reaction rate theory.[30] The choice to deal with the IL as a nonelectrolyte representing the pair cation−anion as a single component with a single collision diameter could appear too crude or not physically correct. Second, the excess Gibbs free energy model chosen here also is derived from theories (local composition theory) that do not consider all aspects of the Coulombic interactions as well as the effect of ion pairing. Despite these conceptual problems, it is surprising how well the Eyring-based model can fit the viscosity of nonaqueous mixtures containing ILs. This behavior is consistent with previous findings,[7−10] again indicating that the ILs exist in the nonaqueous mixtures as a nondissociating component rather than ions.

The Eyring-NRTL and Eyring-UNIQUAC equations tested in this work for IL mixtures are originally applied to polymer[27] and organic molecular[24,25] mixtures, respectively. For systems of nonaqueous mixtures containing ILs, the Eyring-UNIQUAC equation gives lower ADD% than the Eyring-NRTL model. This is very interesting since both NRTL and UNIQUAC equations are theoretically based on a local composition model by assuming that the ratio of species surrounding any molecule also depends on the differences in size and energies of interaction. If we plot both the ADD% of Eyring-NRTL and

Table 2. Results for the One-Parameter Eyring-UNIQUAC and Seddon Equations

system	N	T(K)	ADD [%] Eyring-UNIQUAC (1)	ADD [%] Seddon
[C$_4$mim]BF$_4$−DMF[21]	15	298.15	2.72	12.78
[C$_4$mim]BF$_4$−2-butanone[21]	15	298.15	3.10	11.36
[C$_4$mim]BF$_4$−acetonitrile[32,33]	28	298.15	3.21	17.98
[C$_4$mim]BF$_4$−dichloromethane[32,33]	15	298.15	3.60	20.87
[C$_4$mim]BF$_4$−ethanol[32,33]	13	298.15	4.36	5.92
[C$_8$mim]BF$_4$−dichloromethane[32,33]	15	298.15	5.80	34.61
[C$_8$mim]BF$_4$−2-butanone[32,33]	15	298.15	2.52	16.71
[C$_8$mim]BF$_4$−1-propanol[34]	15	298.15	1.64	6.38
[C$_8$mim]BF$_4$−2-propanol[34]	15	298.15	1.85	7.27
[C$_8$mim]BF$_4$−ethanol[34]	15	298.15	0.82	12.17
[C$_8$mim]BF$_4$−methanol[34]	15	298.15	3.28	19.44
[C$_4$mim]PF$_6$−2-butanone[35]	15	298.15	1.92	7.70
[C$_4$mim]PF$_6$−acetone[35]	15	298.15	1.00	11.30
[C$_4$mim]PF$_6$−acetonitrile[20]	15	298.15	6.49	18.43
[C$_4$mim]PF$_6$−cyclopentanone[35]	15	298.15	1.90	14.10
[C$_4$mim]PF$_6$−DMSO[20]	15	298.15	9.99	21.93
[C$_4$mim]PF$_6$−ethyl acetate[35]	15	298.15	4.89	9.74
[C$_4$mim]PF$_6$−methanol[20]	15	298.15	5.85	13.21
[C$_4$mim]PF$_6$−pentanone[35]	15	298.15	3.58	5.57
[C$_4$mim]PF$_6$−THF[20]	15	298.15	12.19	21.40
[C$_2$mim]EtSO$_4$−ethanol[36]	26	298.15	1.62	14.11
[MTEOA]MeSO$_4$−ethanol[37]	18	298.15	8.19	35.64
[C$_4$mpy]BF$_4$ + methanol[38]	39	298.15−323.15	2.17	14.93
[C$_4$mim]ClO$_4$−ethanol[39]	69	283.15−343.15	7.81	4.07
[C$_8$mim]BF$_4$−ethanol[39]	78	283.15−343.15	8.49	12.29
[C$_8$mim]Cl + 1-propanol[40]	39	298.15−328.15	3.88	8.05
[C$_8$mim]Cl + ethanol[40]	33	298.15−328.15	3.37	7.47
[C$_8$mim]Cl + methanol[40]	45	298.15−328.15	6.68	11.07
[C$_2$mim]EtSO$_4$−1-propanol[41]	33	298.15−328.15	2.41	13.74
[C$_2$mim]EtSO$_4$−2-propanol[41]	33	298.15−328.15	1.55	18.64
[C$_2$mim]EtSO$_4$−methanol[41]	39	298.15−328.15	9.75	25.83
[C$_4$mim]MeSO$_4$−ethanol[42]	39	298.15−328.15	4.67	19.34
[C$_2$mpy]EtSO$_4$ + ethanol[43]	36	298.15−328.15	8.32	13.78
[C$_4$mim]PF$_6$ + MEA[44]	88	288.15−323.15	3.93	7.87
[C$_2$mim]PF$_6$ + DMEA[44]	88	288.15−323.15	6.90	8.81
total	1014		4.58	14.41

Eyring-UNIQUAC equations against the maximum g_E^{Θ} value (for every system the g_E^{Θ}-max values are calculated by eq 6 from the experimental viscosity data) of systems as shown in Figure 1, it will be found that in the area of g_E^{Θ}-max more than 2400 the ADD% of Eyring-NRTL dramatic growth is larger. The phenomena may be attributed to the fact that a global average α value of 0.25 was adapt in the Eyring-NRTL equation. For systems of g_E^{Θ}-max less than 2400 (most IL systems are local at this area in Figure 2), $\alpha = 0.25$ is a good approximate, and the ADD% of Eyring-NRTL is almost the same or even less than the Eyring-UNIQUAC equation. Further tests show that, for systems where g_E^{Θ}-max is larger than 2400, a smaller α value can lead to good results. An example for the system of [C$_8$mim]BF$_4$−methanol with g_E^{Θ}-max of 2756.5 is shown in Figure 2. It could be found that when the α value takes an optimized value of 0.16, the NRTL equation fits the g_E^{Θ} curve far better than α with 0.25. Of course, in that case the Eyring-NRTL equation becomes a three-parameter model. It must be mentioned again that no global suitable value of α can be found for all of the IL systems studied in this work.

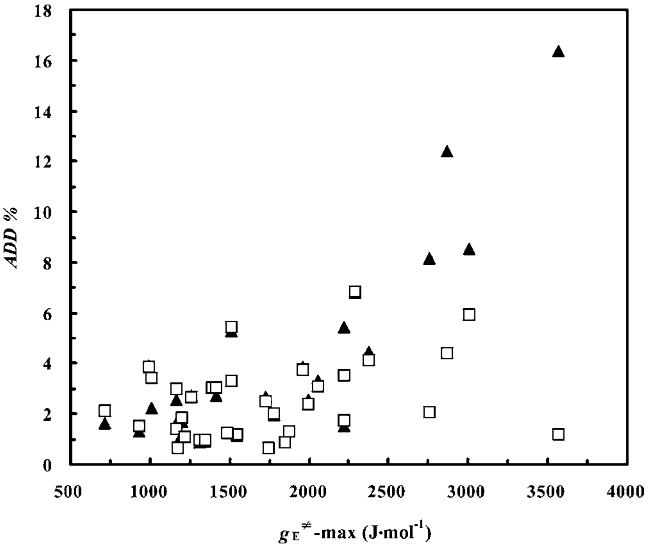

Figure 1. Plot ADD% against $g_E^{\neq}$-max for the Eyring-NRTL equation, ▲; and the Eyring-UNIQUAC equation, □.

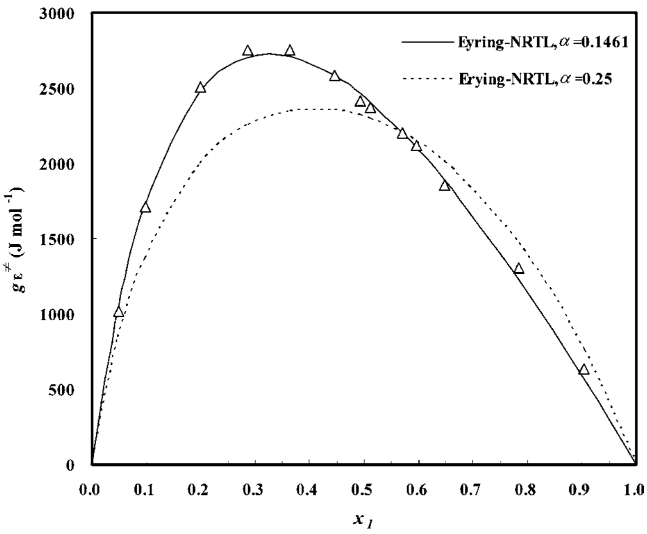

Figure 2. Excess free energy of activation for viscous flow, $g_E^{\neq}$, for 1-methyl-3-octylimidazolium tetrafluoroborate in the methanol system[34] at 298.15 K and its representation by the Eyring-NRTL equation with different *a* values.

The Eyring-UNIQUAC equation describes the viscosity of ILs system quit well with a global ADD% of 2.46 %. It requires for each pure component i a "shape" (relative area) parameter q_i and a "size" (relative volume) parameter r_i. These parameters can be obtained by the group contribution method. The volume and surface group parameters, R_K and Q_K, for groups except for ILs are taken from Poling et al.[45] For the IL species, these parameters were taken directly or derived from the corresponding basic groups from literature.[46−51] It is widely accepted that the UNIQUAC equation has a firm fundamental basis. The UNIQUAC equation contains volume and surface area parameters of the entropic term and the interaction parameters of the enthalpic term. Although the introduction of the entropic term into the equation makes it become algebraically complicated, better results can be obtained in this regard. The larger size differences of the constituent molecules in ILs with cosolvent systems make the entropic contribution become non-neglectable. The Eyring-UNIQUAC equation containing both entropic and enthalpic contributions seems quite suitable for size-asymmetric mixtures containing large and small molecules. Recently, the Eyring-UNIQUAC equation has been successfully applied to modeling organophosphate extractant mixtures which are also characterized as size-asymmetric systems.[52]

The use of the theoretically based model for viscosity modeling of IL mixtures will facilitate the calculation of terminal or bigger systems by only using the binary energy interaction parameters. Very recently, Simoni et al.[13] systematically compared NRTL, eNRTL, and UNIQUAC models to predict ternary LLE of IL systems solely from binary parameters. However, the experimental ternary viscosities of IL systems are extremely scarce, it is not possible to compare the Eyring-NRTL and Eyring-UNIQUAC model in their predicting ability for ternary data from the binary parameters.

Modified Eyring-UNIQUAC Method

The models compared above all have two adjustable parameters at one temperature. However, it frequently happens that experimental viscosity data for a certain binary mixture are so fragmentary that it is impossible to obtain two or three meaningful parameters. Limited experimental data can only yield one significant binary parameter. In that event, it is tempting to use the Seddon equation (one-parameter)[19] for ILs with cosolvent systems. In this section, the Eyring-UNIQUAC equation will be reduced to a one-parameter form through reasonable approximations.

It is well-known that the UNIQUAC equation can be simplified by assuming that

$$u_{11} = \frac{-\Delta U_1}{q_1} \quad \text{and} \quad u_{22} = \frac{-\Delta U_2}{q_2} \tag{15}$$

and that

$$u_{12} = u_{21} = (u_{11}u_{22})^{1/2}(1 - c_{12}) \tag{16}$$

where the energy ΔU_i is given by $\Delta U_i \approx \Delta H_{vi} - RT$, and only c_{12} remains as an adjustable binary parameter. Although the experimental viscosities of ILs are widely available, the experimental studies of heat of vaporization (ΔH_{vi}) have proved to be challenging and have been performed only for a relatively small number of ILs.[53]

So, for the Eyring-UNIQUAC equation used in viscosity correlation, we just assume that

$$u_{12} = u_{21} = u \tag{17}$$

Here only u is an adjustable binary parameter. Then the Eyring-UNIQUAC equation becomes

$$\ln(\eta_{\text{mix}}V_{\text{mix}}) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 \ln\frac{\phi_1}{x_1} + x_2 \ln\frac{\phi_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln\frac{\theta_1}{\phi_1} + q_2 x_2 \ln\frac{\theta_2}{\phi_2}\right) - x_1 q_1 \ln\left(\theta_1 + \theta_2 \exp\left(-\frac{u}{RT}\right)\right) - x_2 q_2 \ln\left(\theta_2 + \theta_1 \exp\left(-\frac{u}{RT}\right)\right) \tag{18}$$

The results for the one-parameter Eyring-UNIQUAC equation are shown in Table 2. For comparison, the results calculated by the Seddon equation[19] are also shown in Table 2. The Seddon equation was widely applied to describe the IL mixture viscosity[20−23] which could be expressed as:

$$\ln \eta_{\text{mix}} = \ln \eta_{\text{IL}} - \frac{x_s}{a} \tag{19}$$

where η_{mix} and η_{IL} are the viscosities of the mixture and pure IL, respectively, x_s is the molar fraction of cosolvent, and a is the empirical constant fitted to the selected IL. When the viscosity data are available at different temperatures, the linear temperature dependence of parameters in eq 12 is also adapted as taken above.

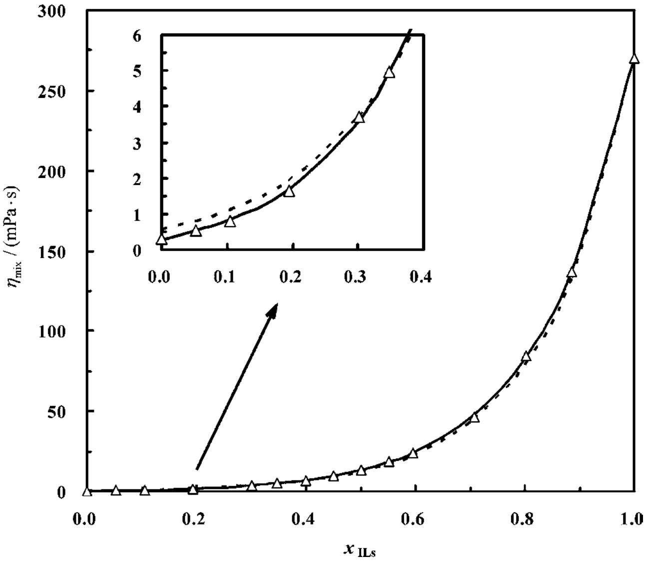

Figure 3. Simplified Eyring-UNIQUAC equation (solid lines, —) and Seddon equation (dotted lines, ---) applied to calculate the viscosities of 1-butyl-3-methylimidazolium hexafluorophosphate with the acetone system[35] at 298.15 K.

The result shows that the one-parameter Eyring-UNIQUAC equation can describe the viscosity well with an ADD% of 4.58 %. On the other hand, the Seddon equation with an ADD% of 14.41 % is much larger than the simplified Eyring-UNIQUAC equation. Figure 3 shows the viscosities of 1-butyl-3-methylimidazolium hexafluorophosphate with acetone[35] from the simplified Eyring-UNIQUAC and Seddon equations, along with the experimental viscosity data, for the 298.15 K case. It is always true that large differences in the values of pure component viscosities can be observed for ILs with cosolvent systems, as in the case of 1-butyl-3-methylimidazolium hexafluorophosphate with acetone shown in Figure 3. The simplified Eyring-UNIQUAC equation shows a good representation of viscosity behavior in this case. When the Seddon equation was used, large differences can be found in the solvent-rich region as shown in Figure 3. It was found that the Seddon equation always gives satisfactory results in the IL-rich region, while in the solvent-rich region this equation gives much larger derivatives. One advantage of the Seddon equation was that this equation can be used to semipredict the viscosities of IL−cosolvent mixtures when the a constant in the Seddon equation was obtained by the experimental data for a certain type of ILs.[19] However, for correlative application the simplified Eyring-UNIQUAC equation will be beneficial in the viscosity calculation for IL−cosolvent mixtures.

Conclusions

In this work, we have evaluated the capability of viscosity models based on Eyring's absolute rate theory and activity coefficient models, namely, the Eyring-NRTL and Eyring-UNIQUAC equations, to nonaqueous mixtures containing ILs. The results were compared and discussed. For the system with large nonideality, the Eyring-NRTL equation needs three adjustable parameters to give satisfactory results, while the two-parameter Eyring-UNIQUAC model could give completely satisfactory results for these systems.

The Eyring-UNIQUAC equation was further simplified to have only one adjustable parameter by suitable assumptions. The simplified one-parameter Eyring-UNIQUAC equation was compared with the Seddon equation. The results show that the one-parameter Eyring-UNIQUAC equation can describe the viscosity well for IL−cosolvent systems. The simplified equation will be beneficial when only limited experimental data are available.

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