Fluid Phase Equilibria 427 (2016) 166–174

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Viscosity estimation of ternary mixtures containing ionic liquid from their binary subsystems: A comparison of three viscosity equations

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ARTICLE INFO

Article history:
Received 27 April 2016
Received in revised form
7 July 2016
Accepted 8 July 2016
Available online 11 July 2016

Keywords:
Ionic liquids
Viscosity
Ternary mixtures
Prediction
Viscosity model

ABSTRACT

Viscosity of the mixture containing ionic liquid (IL) is important for engineering design and application. The modeling of viscosity of the ternary mixtures containing IL is still in its infancy. The aim of this work is to evaluate the predictive ability of the semi-theoretical viscosity equations based on Eyring's absolute rate theory and excess Gibbs free energy model for the ternary mixtures containing IL in terms of the viscosity of their binary subsystems. Three viscosity equations namely Eyring-UNIQUAC, Eyring-NRTL, and Eyring-Wilson equations are employed and extended to estimate the viscosity of ternary mixtures of IL with two molecular solvents using the interaction parameters obtained from their binary subsystems. The results were compared and discussed. The correlation results of the viscosity for 30 binary subsystems with 444 data points show that the Eyring-Wilson equation has more applicability and precision than those of the Eyring-UNIQUAC and Eyring-NRTL equations. Accordingly, the prediction results of the viscosity for 13 ternary mixtures containing IL with 813 data points indicate that the Eyring-Wilson equation has much better predictive ability than that of the Eyring-UNIQUAC and Eyring-NRTL equations. Moreover, the Eyring-Wilson equation can be used to predict the ternary viscosity at other temperature such as 313.15 K using the interaction parameters obtained from their binary subsystems at 298.15 K.

1. Introduction

Ionic liquid (IL) as "designer solvents" has received considerable attention in a variety of industrial applications involving catalytic reactions [1], synthesis [2,3], phase separations [4,5], and acidic gas absorption [6]. Thermodynamic and transport properties of IL such as density, surface tension, thermal decomposition, and viscosity, are very important to the practical application of IL to industrial processes. Among these properties, viscosity is essential for detailed design and optimizing industrial processes, such as heat and mass transfer, separation processes, and reaction engineering. On the other hand, high viscosity of pure IL may be a limiting factor in the industrial application of IL, because under this condition the pumping and energy costs will become prohibitive. In this regard, it is preferred to mix IL with other solvents to overcome this limitation effectively and gain some promising performance during the practical application [7,8]. Moreover, the concentration-dependent viscosity of IL with other solvents is helpful in interpreting intermolecular interaction between IL and solvent based on the viscosity deviations and excess Gibbs energy of activation for viscous flow [9]. Therefore, investigating the viscosity property of the mixture containing IL is crucially important for both the industrial and the academic communities.

It is known that IL usually be mixed with more than one solvent or compound in many practical applications, which will affect the viscosity and performance of the mixtures. For example, the ternary mixture of amine + water + IL system has been studied to achieve lower viscosity of solution, which increases the initial CO_2 absorption rate and directly lowers energy requirements during the absorption of CO_2 [10,11]. Compared with the researches about the viscosity of binary mixtures containing IL, few studies concerning the viscosity of ternary mixtures of IL with two solvents have been made in the past few years. To obtain the viscosity of ternary mixtures containing IL, the experimental measurement is indispensably important. However, it is always not practical to

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http://dx.doi.org/10.1016/j.fluid.2016.07.010
0378-3812/

experimentally determine the viscosity at every imaginable composition, because of the large amounts of possible combination of ternary mixtures of IL with two solvents. Besides, the experimental measurement is not always possible, in some case it is time consuming and relatively expensive. Therefore, developing predictive methods to obtain the viscosity of ternary mixtures containing IL is extremely important. To this end, scientists and engineers have attempted to develop reliable and accurate predictive models to estimate the viscosity of ternary mixtures containing IL [12–14]. For example, Lashkarblooki et al. [12] proposed a multi-layer feed-forward artificial neural network (ANN) model to estimate the viscosity of ternary mixtures containing IL as a function of boiling points, molecular weight of species, and compositions of the ternary system, and the results demonstrated that the proposed ANN model was able to predict the ternary viscosity, which were helpful for engineering and optimization calculations. However, according to the description of the ANN model proposed by Lashkarblooki and co-workers [12], one can see that the proposed ANN model needs more than half of the experimental viscosity data as the training data set to generate the ANN structure and find the optimum parameters of network including one hidden layer with 12 neurons. Accordingly, the ANN model may not be suitable for the new ternary systems due to the lack of the experimental viscosity data. Moreover, the ANN model may not be used for predictive purpose if the input data are outside the range used for developing the model. Therefore, it is crucial to develop a predictive model to estimate the viscosity of ternary mixtures containing IL directly.

Recently, some empirical [15] and semi-theoretical [16–21] models have been proposed for viscosity modeling of binary mixtures of IL with co-solvent, among which the semi-theoretical viscosity equations based on Eyring's absolute rate theory and excess Gibbs free energy model have shown a good ability of correlating the viscosity of IL-solvent binary mixtures [16–19]. For example, the Eyring-UNIQUAC and Eyring-NRTL equations were employed by Wang and co-workers to correlate the viscosity of IL-solvent mixtures [17], indicating that the two-parameter Eyring-UNIQUAC equation could give complete satisfactory results like the three-parameter Eyring-NRTL equation. Recently, the Eyring-Wilson equation based on Eyring's absolute rate theory and the minus form of the Wilson activity coefficient model proposed by He et al. has been successfully applied to correlate the viscosity of IL-solvent binary mixtures [18], showing that the Eyring-Wilson equation can give almost the same results as the Eyring-UNIQUAC equation, and better than those of the Eyring-NRTL equation. By analyzing the above three viscosity equations, it can be found that they have the ability to estimate the viscosity data of the ternary mixtures containing IL in terms of the viscosity of their binary subsystems, which is an advantage, comparing with other empirical viscosity equation [15]. It is, therefore, the purpose of the present study to investigate the applicability of the semi-theoretical viscosity equations based on Eyring's absolute rate theory and excess Gibbs free energy model to estimate viscosity of ternary mixtures containing IL in terms of the viscosity of their binary subsystems. The viscosity equations tested in this work include the Eyring-UNIQUAC, Eyring-NRTL, and Eyring-Wilson equations. Specific ideas as follows: Firstly, viscosity data of the binary subsystems of ternary mixtures obtained from the previously public shed literatures are correlated through the above viscosity equations, respectively. Afterwards, viscosity data of the ternary mixtures containing IL are estimated by the above viscosity equations using the interaction parameters obtained from their binary subsystems. Finally, the prediction viscosity data are compared with the experimental ones obtained from the literature to evaluate the predictive capability of the above three viscosity equations. The results show that the Eyring-Wilson equation can better predict viscosity of ternary mixtures containing IL in terms of the viscosity of their binary subsystems than Eyring-UNIQUAC and Eyring-NRTL equations.

2. Methodology

2.1. Data set

Reliable experimental data points are vital for developing and checking prediction models. In this study, viscosity data of the studied ternary mixtures of IL with two molecular solvents at different composition were gathered from 11 references (the reference numbers see Table 2), including 13 ternary mixtures (total 813 data points). The anions of the investigated ILs contained bis(trifluoromethylsulfonyl)imide [BTI], alkyl sulfate [RSO_4], dicyanamide [DCA], and acetate [OAC], and the cations were imidazolium [Im] and tris(2-hydroxyethyl) methylammonium [MEDA]. The molecular components of the mixtures are commonly used solvents, including water, alcohols, and esters.

2.2. Viscosity equation

According to Eyring's absolute rate theory, viscous flow of liquids can be regarded as an activated process [22]. By the application of the Eyring's absolute rate theory [23–26], the viscosity of nonideal solution can be expressed as:

$$\ln(\eta_{\mathrm{mix}}V_{\mathrm{mix}}) = \sum_{i=1}^{K} x_i \ln(\eta_i V_i) + \frac{g_{\mathrm{E}}^{\neq}}{RT} \tag{1}$$

where η, V, and x are the dynamic viscosity, the molar volume, and the mole fraction of compounds, respectively. Subscript mix and i stand for the mixture and component, respectively. K is the number of components. $g_{\mathrm{E}}^{\neq}$ is the excess molar free energy of activation for flow, which is a close analogy to the respective excess molar free energy of mixing [17]. R is the gas constant and T is the Kelvin temperature. V_{mix} of the mixtures can be calculated from the molar volume of pure components as follows:

$$V_{\mathrm{mix}} = \sum_{i=1}^{K} x_i V_i \tag{2}$$

In the last decade, many studies have revealed that $g_{\mathrm{E}}^{\neq}/RT$ in Eq (1) could function by any form of the excess Gibbs free energy function [23–26]. The Eyring-UNIQUAC equation developed by Martins et al. [23,24] for organic molecular mixtures uses the UNIQUAC model to describe $g_{\mathrm{E}}^{\neq}/RT$ in Eq (1) and has the final form for mixtures as:

$$\ln(\eta_{\mathrm{mix}}V_{\mathrm{mix}}) = \sum_{i=1}^{K} x_i \ln(\eta_i V_i) + \sum_{i=1}^{K} x_i \ln\frac{\phi_i}{x_i} + \frac{z}{2}\sum_{i=1}^{K} q_i x_i \ln\frac{\theta_i}{\phi_i} - \sum_{i=1}^{K} q_i x_i \ln\left(\sum_{j=1}^{K}\theta_j \tau_{ji}\right) \tag{3}$$

and

$$\tau_{ji} = \exp\left[-\left(g_{ji} - g_{ii}\right)\Big/RT\right] \tag{4}$$

where q_i is the surface area parameter, θ_i is the surface area fraction, ϕ_i is the volume fraction, τ_{ji} is the interaction parameter between