Journal of Molecular Liquids xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Toward a predictive model for estimating viscosity of ternary mixtures containing ionic liquids

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ARTICLE INFO

Article history:
Received 10 August 2014
Accepted 24 October 2014
Available online xxxx

Keywords:
Ionic liquids
Viscosity
Least square support vector machine
Coupled simulated annealing
Leverage approach

ABSTRACT

Ionic liquids (ILs) are widely under research and being more and more used in many industrial fields due to their unique properties. The knowledge of physicochemical properties of ILs is vital for their applications. Viscosity is one of the most important physical properties of ILs. Since the experimental measurement of viscosity is expensive, time consuming and cumbersome, seeking for a reliable and accurate model for predicting the viscosity of IL mixtures is essential. To this end, a large data bank, covering a wide range of ternary mixtures containing ILs, was collected from open literature sources. Afterwards, a rigorous modeling approach, namely least square support vector machine (LSSVM) was employed to predict the viscosity of ternary mixtures. The parameters of the model were optimized using coupled simulated annealing (CSA) optimization tool. The inputs of the model are boiling point temperature, molecular weight and composition of mixture compounds. Statistical and graphical error analyses indicated that the developed model can satisfactorily predict ternary mixture viscosity. Moreover, it was demonstrated that the proposed model is able to predict the actual physical trend of viscosity with variation of molecular weight and boiling point of ILs, ethanol content and water content. Furthermore, the relevancy factor demonstrated that the average boiling point of the ternary mixture has the greatest impact on the viscosity. Finally, the Leverage approach was performed, in which the statistical Hat matrix, Williams Plot, and the residuals of the model results led to recognition of the probable outliers. All the experimental data seem to be reliable except five data points. Thus, the developed model could be reliable for the prediction of ternary mixture viscosity in its applicability domain.

1. Introduction

Ionic liquids (ILs) are defined as salts that have melting points under 100 °C and are liquid in a wide range of temperature [1,2]. Ionic liquids have the features of classical salts such as high polarity, chemical and thermal stability, flame resistance [3–7], recyclability, high solubility, nonvolatility, heat hardiness and conduction properties [8–14], while they are liquid in ambient temperature, leading to draw considerable attention from many fields such as electrolytes in batteries [14], lubricant agents [14], catalysts [15,16], liquid–liquid extraction media [16] and separation processes [14,17]. Moreover, ILs are introduced as "solvent designers" [1,18], because they can be designed to have desired properties by suitable selection of the anion and cation or by manipulation of branching length during ILs' synthesis. The cation part of ILs is organic such as imidazolium, quaternary ammonium, phosphonium and pyridinium, while the anion part can be organic/inorganic such as tetrafluoroborate, hexafluorophosphate, trifluoromethanesulfonate and bis (trifluoromethylsulfonyl) amide [1,19–25].

Physical and chemical properties of ILs are important for their design and use in the aforementioned applications [26]. Viscosity is one of the most significant properties, which has been widely used to study ILs and their purity [27–31]. Viscosity is a transport property which is caused by the friction among neighboring particles in a fluid that are moving at different velocities. In other words, this property provides a measure of fluid resistance to gradual deformation by shear stress or tensile stress. The viscosity plays a crucial role in fluid flow, mass transfer and heat transfer calculations [32–34]; therefore, in order to deal with a fluid in industrial processes (such as heat-transfer equipment, piping, liquid–liquid extractors, reactors, stripping columns, crystallization equipment, and distillation columns), knowing viscosity value is of a great importance [20]. One of the disadvantages of ILs is their higher viscosity compared to conventional organic solvents, because it adversely affects mass transfer and power requirements [1,35,36]. Since the ILs can be custom designed, their viscosity covers a wide range. The viscosities of ILs are strongly dependent on the amount of dissolved water [37]. Pure ILs may have some limitations. In order to achieve more or various properties, ILs may be mixed with other compounds. Thus, binary and ternary IL mixtures which extend ILs' applications are more interesting [38].

Although since the last decade many researchers have measured physicochemical properties of ILs, experimental measurements have

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http://dx.doi.org/10.1016/j.molliq.2014.10.033
0167-7322/

not been adequate [36,39–41]. Experimental measurements in many cases are costly, time consuming and cumbersome. These difficulties are greater for ILs due to the diversity of anion–cation combinations [35,42] (about 10^{18} potential anion–cation combinations [43]). Therefore, searching for a quick and accurate method for the determination of ILs properties is inevitable. To this end, several researchers have attempted to develop reliable and accurate models for predicting the properties of IL mixtures.

IL mixtures are not analytically described in the literature as thoroughly as their pure state [44,45]. Many analytical techniques have been employed to predict thermo-physical properties. In semi-empirical methods such as group contribution, enough experimental data is required. Moreover, molecular dynamics simulation has been used in several papers to calculate viscosity [39,40,46,47]. Furthermore, group contribution method has been applied to predict viscosity by several researchers [20,48–50]. Gharagheizi et al. [48] used a group contribution method for 46 sub-structures to estimate the viscosity of ILs. The proposed model produces a low average relative deviation (AARD) of less than 6.4%. Daniel et al. [49] proposed a group contribution method to predict the viscosity at different temperatures of magnetic ionic liquids (MILs). Their model exhibited a good agreement with the experimental results and presented a percentage deviation of 7.64%. Bajić et al. [30] used two different approaches, group contribution models (UNIFAC-VISCO and ASOG-VISCO) and correlations (Seddon, Grunberg–Nissan, McAlister, Eyring-UNIQUAC and Eyring-NRTL models) to calculate viscosities of ten binary liquid mixtures consisting of ILs and organic compounds in a wide temperature range.

Some researchers have developed quantitative structure property relationships (QSPR) as prediction models for thermo-physical properties such as melting point [43,51], density [52], viscosity [3,35,36,53,54], and conductivity [3,54] of ILs. Chen et al. [35] developed a correlation and simplified QSPR coupled with the descriptors of group contribution for viscosity of imidazolium-based ILs. They obtained a relationship between the descriptive parameters and the viscosity of imidazolium-based ILs. Yu et al. [36] obtained eight QSPR correlations for viscosities of bis (trifluoromethylsulfonyl) imide-based ILs at 283 K, 293 K, 298 K, 303 K, 313 K, 323 K, 333 K and 343 K.

In recent years, few studies have been carried out to predict viscosity of IL mixtures [30,42,55,56]. Unlike pure ILs, very few works have studied the thermo-physical properties of ternary mixtures of ILs. Diaz-Rodriguez et al. [55] employed an artificial neural network multilayer perceptron (MLP) model to estimate viscosity of ILs. They reported mean prediction errors around 1.5% for a k-fold cross-validation and about 2.3% for three blind tests. Fatehi et al. [56] estimated the viscosity of binary mixtures of ILs and solvents based on the structure groups of the ionic liquid using an artificial neural network. They concluded that their result was capable to estimate the viscosity of binary mixtures, including a range of ionic liquids and solvents, with an average relative error of 0.6%. The main objective of this study is to propose a robust soft computing modeling approach, namely least square support vector machine (LSSVM) for accurate viscosity prediction of ternary mixtures contacting ILs. The parameters of the LSSVM model are optimized using a novel feature selection mechanism based on coupled simulated annealing (CSA). To this end, the following are the objectives of this study:

1. To acquire a comprehensive and large data bank, covering a wide range of ternary mixtures containing ILs from open literature sources.
2. To develop a novel, accurate and robust intelligent model based on LSSVM modeling approach for prediction of viscosity of ternary mixtures containing ILs.
3. To evaluate the performance of the developed model for predicting viscosity of ternary mixtures containing ILs using graphical and statistical error analyses.
4. To validate the developed model by calculating viscosity of ternary mixtures containing ILs as a function of input parameters to see whether the proposed model follows the expected physical trends.
5. To investigate the applicability domain of the applied model based on the Leverage approach.
6. To investigate the relative impact of each input parameter on viscosity of ternary mixtures containing ILs using the relevancy factor.

2. Data collection

Reliability and robustness of a model/correlation for prediction of a given property strongly depends on the comprehensiveness of the used dataset for its development. In this study, almost all experimental viscosity data of ternary mixtures containing IL data sets, which are available in open literature sources, have been used [57–65]. The properties of the studied compounds are summarized in Table 1. The next step is to determine the input variables (independent variables) for model development. Molecular weight (Mw) and boiling point (T_b) of the components as well as the composition of non-IL substances were selected as the input variables to distinguish the diverse species. The viscosity of mixtures containing ILs has been considered as the desirable output. Therefore, the following general relation has been considered for the ternary viscosity of ILs:

$$\mu = f(Mw_i, Tb_i, X_2, X_3). \quad (1)$$

The used data in this study covers a wide range of IL mixtures, and consequently, the developed model based on these data could be reliable and efficient for predicting viscosity of other IL mixtures.

3. Model development

3.1. Least square support vector machine

One of the most robust and consistent strategy developed from machine learning community is the Support Vector Machine, which recently has been applied in many fields [33,66,67]. This algorithm as a tool for a set of related supervised learning methods can be employed not only for data analyzing and patterns recognizing, but also for regression analysis. Based on SVM principles, any function $f(x)$ can be expressed as follows [68]:

$$f(x) = w^T \varphi(x) + b \quad (2)$$

where w^T and $\varphi(x)$ are the transposed output layer vector and the kernel function, respectively, and b is the bias. The input of the model (x) has a dimension of $N \times n$, where N and n represent the number of data points

Table 1
The physicochemical properties of ionic and non-ionic compounds.

Component	Molar weight (g/gmol)	Boiling point (K)	Ref.
Water	18.01	373.15	[89]
Ethanol	46.06	352.2	[89]
1-Propanol	60.09	370.3	[89]
Ethyl ethanoate	88.1	350.2	[89]
2-Propanol	60.09	345.55	[89]
1-Methylethyl ethanoate	102.13	361.73	[89]
Ethyl 1,1-dimethylethyl ether	102.17	346.3	[89]
Methanol	32.04	338.0	[89]
1-Octyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl]imide	475.5	954.0	[65]
1-Butyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl]imide	419.4	862.4	[65]
1-Ethyl-3-methylimidazolium ethyl sulfate	236.3	712.7	[65]
1,3-Dimethylimidazolium methylsulfate	208.2	666.9	[65]
1-Butyl-3-methylimidazolium methylsulfate	250.3	735.6	[65]

Please cite this article as: M. Hossein-Zadeh, A. Hemmati-Sarapardeh, Toward a predictive model for estimating viscosity of ternary mixtures containing ionic liquids, J. Mol. Liq. (2014), http://dx.doi.org/10.1016/j.molliq.2014.10.033