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A robust modeling approach to predict the surface tension of ionic liquids

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ABSTRACT

The objective of the present study is to develop a mathematical model based on the least square support vector machine to predict the surface tension of ionic liquids (ILs). Molecular weight, reduced temperature, reduced pressure, critical compressibility factor and acentric factor are selected as input parameters and the surface tension is designated as the output parameter. An extensive database including 868 experimental data points for surface tension of 61 ILs are considered to develop the LSSVM model which the adjustable parameters of the model are calculated by a genetic algorithm programming. The proposed model exhibits good accuracy with the average absolute relative deviation of 1.41, 1.74 and 1.54% for train set, test set, and total data, respectively. The Leverage method is employed to check the validity of the model. The results show that the majority of data points are located in a standard error domain demonstrating statistical acceptability of the model and only 3.6% of data points are recognized as suspected data. To evaluate the effects of input parameters on the surface tension of ILs, a sensitivity analysis is performed. The results show that the critical compressibility factor of ILs with relative importance of 22.97% has the greatest effect on the surface tension of ionic liquids. Finally, the effects of temperature and the total number of carbon in cation side alkyl chain on the surface tension are

Abbreviations: [2-HC_2C_2A][HCO2], 2-hydroxydiethylammonium formate; [$C_6C_6C_6C_{14}P$][Cl], trihexyltetradecylphosphonium chloride; [$C_6C_6C_6C_{14}P$][NTf2], trihexyltetradecylphosphoniumbis[(trifluoromethyl)sulfonyl]imide; [$C_4C_1C_1$im] [PF6], 1-butyl-2,3-dimethylimidazolium hexafluorophosphate; [$C_4C_1C_1$im][NTf2], 1-butyl-2,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_4C_1im] [TfO], 1-butyl-3-methylimidazolium trifluoromethanesulfonate; [C_4C_1im][BF4], 1-butyl-3-methylimidazolium tetrafluoroborate; [C_4C_1im][Cl], 1-butyl-3-methylimidazolium chloride; [C_4C_1im][dca], 1-butyl-3-methylimidazolium dicyanamide; [C_4C_1im][I], 1-butyl-3-methylimidazolium iodide; [C_4C_1im][MSO4], 1-butyl-3-methylimidazolium methylsulfate; [C_4C_1im][NTf2], 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_4C_1im][PF6], 1-butyl-3-methylimidazolium hexafluorophosphate; [C_4C_1im][tca], 1-butyl-3-methylimidazolium thiocyanate; [C_4C_1py] [NTf2], 1-butyl-3-methylpyridinium Bis(trifluoromethylsulfonyl)imide; [C_4C_1pyr][NTf2], 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide; [$C_{10}C_{10}$im] [NTf2], 1,3-didecylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_1C_1im] [NTf2], 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_2C_2im] [NTf2], 1,3-diethylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_2OHmim][BF4], 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate; [C_3C_3im] [NTf2], 1,3-dipropylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_4C_4im] [NTf2], 1,3-dibutylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_5C_5im] [NTf2], 1,3-dipentylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_6C_6im] [NTf2], 1,3-dihexylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_7C_7im] [NTf2], 1,3-diheptylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_8C_8im] [NTf2], 1,3-dioctylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_9C_9im] [NTf2], 1,3-dinonylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_1C_1im] [MSO4], 1,3-dimethylimidazolium methylsulfate; [C_2 C_1im] [TfO], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate; [C_2 C_1im][BF4], 1-ethyl-3-methylimidazolium tetrafluoroborate; [C_2 C_1im][dca], 1-ethyl-3-methylimidazolium dicyanamide; [C_2 C_1im][ESO4], 1-ethyl-3-methylimidazolium ethylsulfate; [C_2C_1im][NTf2], 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_6C_1im][BF4], 1-hexyl-3-methylimidazolium tetrafluoroborate; [C_6C_1im][Cl], 1-hexyl-3-methylimidazolium chloride; [C_6C_1im][NTf2], 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_6C_1im][PF6], 1-hexyl-3-methylimidazolium hexafluorophosphate; [C_7C_1im] [NTf2], 1-heptyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_7y][NTf2], 1-hexylpyridinium bis[(trifluoromethyl)sulfonyl]imide; [C_1C_4py][BF4], 1-butyl-4-methylpyridinium tetrafluoroborate; [C_1C_4py][NTf2], 1-butyl-4-methylpyridinium bis[(trifluoromethyl)sulfonyl]imide; [C_1C_4pyr][dca], *n*-methyl-*n*-butylpyrrolidiniumdicyanamide; [C_1C_4py][BF4], 2-methyl-*N*-butylpyridinium tetrafluoroborate; [$C_1C_1C_{10}$N][NTf2], trimethyldecylammoniumbis[(trifluoromethyl)sulfonyl]imide; [$C_1C_1C_4$N] [NTf2], trimethylbutylammoniumbis[(trifluoromethyl)sulfonyl]imide; [$C_1C_1C_6$N][NTf2], trimethylhexylammoniumbis[(trifluoromethyl)sulfonyl]imide; [$C_1C_3C_4$N][NTf2], dimethylpropylbutylammoniumbis[(trifluoromethyl)sulfonyl]imide; [$C_1C_1C_3C_6$N][NTf2], dimethylhexyl(i-propyl)ammoniumbis[(trifluoromethyl)sulfonyl]imide; [$C_2C_2C_2C_6$N][NTf2], triethylhexylammoniumbis[(trifluoromethyl)sulfonyl]imide; [$C_1C_1C_8$N] [NTf2], trimethyloctylammoniumbis[(trifluoromethyl)sulfonyl]imide; [C_2py][NTf2], 1-ethylpyridinium bis[(trifluoromethyl)sulfonyl]imide; [C_8C_1im] [NTf2], 1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_8C_1im][BF4], 1-octyl-3-methylimidazolium tetrafluoroborate; [C_8C_1im][Cl], 1-octyl-3-methylimidazolium chloride; [C_8C_1im][PF6], 1-octyl-3-methylimidazolium hexafluorophosphate; [$C_4C_4C_4C_2$P][DEP], tributyl(ethyl)phosphoniumdiethylphosphate; [C_5C_1im][NTf2], 1-pentyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_3C_1im][BF4], 1-propyl-3-methylimidazolium tetrafluoroborate; [C_3C_1im][NTf2], 1-propyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [C_3C_1im][PF6], 1-propyl-3-methylimidazolium hexafluorophosphate; [C_3C_1py][NTf2], 3-methyl-1-propylpyridinium bis[(trifluoromethyl)sulfonyl]imide; [C_2OHC_1im][BF4], 1-ethanol-3-methylimidazolium tetrafluoroborate; IL, ionic liquid; CF, cost function; LSSVM, least square support vector machine; GA, genetic algorithm; GMDH-PNN, group method of data handling type polynomial neural network; ANN, artificial neural network; RBF, radial basis function; ARD, average relative deviation; AARD, average absolute relative deviation; RMSE, root of mean square error; SD, standard deviation; SA, sensitivity analysis; GCM, group contribution method; CACL, critical alkyl chain length size; QSPR, quantitative structure–property relationship.

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predicted by the proposed model. The model exhibits a monotonic decrease for surface tension with increasing temperature. Moreover, it well predicts the effects of the total number of carbon atoms in cation side alkyl chain on the surface tension.

1. Introduction

The interest in green chemical technology has led to a significant attention of scientific communities to ionic liquids (ILs) [1]. Ionic liquids as a especial class of liquids are organic salts consisted of several organic cations and inorganic or organic anions [2]. Ionic liquids have unique and exceptional properties such as negligible vapor pressure, ease of recycling, nonflammability, unique permittivity, high solvability capacity for both organic and inorganic compounds, high electrical conductivity, and good thermal/chemical/electrochemical stability [3,4]. Such remarkable properties have led to implementation of ILs in different applications including chemical synthesis, catalytic reactions, biotechnology, lubricants, membrane separation technology, and electrolytes in batteries [1,3,4].

In order to apply ILs in different process, understanding their physical properties such as density, viscosity, thermal conductivity, heat capacity, and also surface tension is of great importance. Surface tension is an important property to study the chemistry and physics of free surfaces [5]. For example, at a vapor-liquid interface, surface tension affects the transfer rate of vapor absorption [5,6]. Thus, it plays a key role in process design and is crucial for both scientific and industrial applications.

The surface tension of an IL can be measured experimentally or be predicted by a model. However, experimental surface tension data for pure ILs is rare. In addition, experimental investigation of surface tension for a wide range of temperature is time consuming and expensive [6]. In this regard, development of models to predict the surface tension of different ILs for a broad range of temperature is demanding. In the literature, there are a few methods available to predict the surface tension of ILs but most of them have been developed for a very limited number of ILs and are not mostly accurate enough (see Section 2 for more detailed information).

Over the recent years, computational intelligence schemes such as artificial neural networks (ANNs) have been applied for modeling complex and highly nonlinear problems [7]. Different applications and comprehensive descriptions of ANNs have been provided in the literature [8,9]. In general, ANNs have also considerably attracted researchers' attention to model physicochemical properties of pure and mixture of ILs including thermal conductivity [1], viscosity [10], solubility [11,12], electrical conductivity [13], heat capacity [14], and density [15]. Although ANNs are powerful tools with high degree of flexibility, they have some disadvantages. For instance, when ANNs are used to solve problems, a high number of adjustable parameters needs to be dealt with and the obtained mathematical structure is extremely complex [16]. Besides, overfitting and also difficulties in finding the global minimum for the cost function are still the challenging issues [17–19].

A robust soft computing approach, support vector machine (SVM) [20], has recently attracted especial attention for regression, pattern recognition, and classification problems [21–25]. Support vector machine has a sturdy theoretical concept based on the statistical learning theory. The structural risk minimization (SRM) rule is applied in SVMs in lieu of the conventional empirical risk minimization rule (ERM) used in classical methods (such as ANNs) [17]. Such a pattern makes SVMs thoroughly resistant to the under-fitting and over-fitting issues [26]. In addition, SVM is commonly solved based on quadratic programming (QP). Because QP function has a convex form, only one global and unique solution is achieved which has more advantages than neural networks with abounding local solutions. More benefits of SVM in comparison to ANNs are described in the literature [27,28]. Very recently, we have successfully developed a least square support vector machine (LLSVM) to model the thermal conductivity of 22 ILs. The average absolute relative deviation of the model was only 1.03% indicating excellent accuracy of the proposed model [29].

The objective of the present study is to develop an accurate model to predict the surface tension of a wide range of ILs. In this regard, 868 experimental data points from 61 ILs are considered to develop the model. The LSSVM is implemented to model the experimental data. Molecular weight, reduced temperature, reduced pressure, critical compressibility factor and acentric factor are selected as input parameters and surface tension is designated as the model output. The performance of the model is compared with some other available methods in the literature. In addition, in depth investigation of the proposed model is conducted by statistical analyses including sensitivity analysis and Leverage method.

2. Methodology

2.1. Models for prediction/correlation of surface tension

A few general models have been developed to predict the surface tension of pure ILs which are briefly reviewed in this section.

The most popular simple model to predict the surface tension of ILs is Parachor method [30]:

$$\sigma = \left(\frac{P\rho}{M_W}\right)^4 \tag{1}$$

where P is called "parachor" constant, ρ is density, and M_W is molecular weight. First, Deetlefts et al. [30] employed this formula to predict the surface tension of ILs. It should be noted that, they used group contribution method (GCM) of Knotts et al. [31] in order to determine parachor constants for ILs. However, they have only evaluated Eq. (1) for 9 ILs. Then, some other studies have been conducted based on Eq. (1). For instance, Gardas and Coutinho [32] developed a quantitative structure–property relationship (QSPR) by implementing the GCM method of Knotts et al. to determine parachor constants of ILs in Eq. (1). They have considered 38 imidazolium based ILs and 361 experimental data points for model development in which the average absolute relative deviation (AARD) of the proposed model was 5.75%. Besides the low accuracy of the proposed model, its main limitation was sole applicability to imidazolium based ILs.

As another attempt, Ghasemian and Zobeydi [5] employed Eq. (1) to predict the surface tension of 60 imidazolium based ILs using 209 experimental data points while the AARD of their model was about 8.5%. It should be noted that they have employed GCM method of Valdremma et al. [33–36] to predict the density of pure IL in Eq. (1). The proposed model had also two drawbacks: (i) it was limited to solely imidazolium based ILs, and (ii) had relatively high AARD (%).

Based on the corresponding state principle, Mousazadeh and Faramarzi [37] suggested the following correlation to predict the surface tension of ILs:

$$\sigma = \left[0.5\frac{\sigma_m}{T_b} - 0.819\frac{\sigma_m}{T_b - T_m}\right]T + 0.819\left(\frac{\sigma_m T_b}{T_b - T_m}\right) \tag{2}$$

where σ_m is surface tension at the melting point, T_m is melting temperature, and T_b is boiling temperature. However, it should be noted that it is difficult to measure the surface tension at the melting point for a wide range of ILs. Moreover, the measured surface tension data at the melting point was accompanied by high uncertainty [6].