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Predicting the surface tensions of ionic liquids by the quantitative structure property relationship method using a topological index

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HIGHLIGHTS

- A general topological index was proposed based on atom characters and position.
- The index was extended to predict temperature dependent property of ILs.
- Temperature dependence of QSPR model was correlated with structure parameters.

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ABSTRACT

The general topological indexes (*TIs*) proposed in our previous work were applied to predict the surface tensions of ionic liquids (ILs) by Quantitative Structure Property Relationship (QSPR) method. ILs are a class of molten salts which are composed entirely of cations and anions, therefore the descriptors for ILs are generally calculated from cations and anions separately and the interaction between them is always neglected. In this study, besides the two sets of *TIs* generated from cation and anion, a third *TI* was used to depict the interaction of anion and cation. Differing from the previous estimation methods for surface tensions of ILs, the temperature dependence is also correlated by structure parameters. 930 surface tension data points for 115 ILs are applied to develop QSPR model. The correlation coefficient (R^2) and the overall average absolute deviation (AAD) are 0.9516 and 3.43%, respectively.

1. Introduction

Ionic liquids (ILs) have attracted much attention in recent years, for their beneficial properties such as negligible vapor pressure, high heat capacity, high density, high thermal conductivity, high thermal stability, a wide temperature range for liquid and so on. The fundamental understanding of the physical and chemical properties of ILs is of essential importance. The surface tension of ILs is an important physical property. It is used to access the intrinsic energetics that are involved in the interactions between the ions (Tariq et al., 2012). It is also a powerful means to explore the different types of segregation/orientation that occur at an ionic/molecular level and the interactions with other molecules (Xiao and Malhotra, 2004). Some derived physicochemical properties of the pure ILs were obtained (Wei et al., 2010) according to the relationship between surface tension and temperature. Although some surface tension data are available from literature, there is no comprehensive database publicly available for researchers due to the lack of experimental data for the large number of ILs. Apart from experiments, estimation is a valuable approach to determine the surface tension data.

A number of models have been developed to estimate the surface tension of ILs. These models are mainly classified into two methods: property-based correlation and structure-based estimation.

1.1. Property-based correlation

The surface tension can be correlated to other experimental properties (e.g., density, viscosity, and boiling point) in property-based correlation.

Eq. (1) expressed temperature-independent relationship between surface tension, σ, and density, ρ(Gardas and Coutinho, 2008).

$$\sigma = \left(\frac{P_{ch} \times \rho}{M_w}\right)^4 \quad (1)$$

where M_w is molecular weight, ρ is density, and P_{ch} is parachor.

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Ghatee et al. (2010) proposed that the surface tension can be related to the viscosity as:

$$\ln \sigma = \ln C + D\left(\frac{1}{\eta}\right)^{\phi} \quad (2)$$

where $\ln C$ and D are constants, which are dependent on the substances, and independent of the thermodynamic state of the system; η is the viscosity;and Φ is the universal exponent.

Mousazadeh and Faramarzi (2011) correlated the surface tension with temperature by corresponding states theory.

$$\sigma = 0.849\left(\frac{T_b - T}{T_b - T_m}\right)\delta_m + 0.5\left(\frac{T}{T_b}\right)\delta_m \quad (3)$$

where σ_m is the surface tension at the melting temperature, T_m, and T_b is the boiling temperature. This model relies on σ_m, T_m and T_b.

These methods above rely on other property data, which are also scarce for ILs, therefore the surface tension data can be obtained only if the according properties are known.

1.2. Structure-based estimation

Structure-based method, such as Quantitative Structure Property Relationship (QSPR) and group contribution method are widely used for predicting the properties of ILs. A few structure-based models have been developed for estimating the surface tension of ILs.

Wu et al. (2012) developed a corresponding-states group-contribution method for estimating surface tension of ionic liquids. The critical temperature T_c was abstained from group contribution method.

Mirkhani et al. (2013) developed linear (AAD, 4.9%) and non-linear (AAD, 1.05%) models to predict the surface tensions of ILs. Due to the fact that surface tension of ILs are perfectly linear with temperature, the gradient was set as a constant in the linear model, which is shown as follows.

$$\sigma = 0.08258 - 5.26608 \times 10^{-5} T + \sigma_{Anion} + \sigma_{Cation} \quad (4)$$

where σ_{Anion} and σ_{Cation} are the anion and cation contributions.

A reliable group contribution method (AAD, 3.6%) is developed by Gharagheizi et al. (2012) for the estimation of surface tension of 51 ILs. The model is as follows:

$$\sigma = a + bT + \sigma_{Anion} + \sigma_{Cation} \quad (5)$$

where σ_{Anion} and σ_{Cation} are the anion and cation contributions, a and b are constants.

In the above two models, the gradients were both set as constants, which are unrelated to the molecular structures of ILs. However, the gradients are not the same for most of the ILs, which will be discussed in the next part. It is much more advisable to use different gradients b based on the molecule structures.

In this work, we developed a QSPR model by the topological index (*TI*) proposed in our group. It has been used for predicting the decomposition temperature of ILs (Yan et al., 2012a), the toxicity of ILs in acetylcholin esterase (Yan et al., 2012b) and Leukemia Rat Cell Line (Yan et al., 2012c). The aim of this work is modifying the QSPR model to predict the surface tension of ILs. Also, the *TI* proposed by us was extended to predict the temperature dependent property of ILs.

2. Method

2.1. Data set

A total of 930 data points for 115 ILs were used for developing the QSPR model, which includes 87 imidazoulium (Im), 10 pyridinium (Py), 8 ammonium (Am), 2 pyrrolidinium (Pyr), 4 phosphonium (P), 4 guanidinium (Gu). All data were obtained from literatures that have been reviewed by Tariq et al. (2012). The surface tension data, the corresponding temperatures and the names of ILs are presented in the supplementary material.

2.2. QSPR model

The surface tension of ILs is perfectly linear with temperature and it can be correlated with temperature as follows:

$$\sigma = a + bT \quad (6)$$

where a and b are parameters. The correlation coefficients (R^2) of Eq. (6) are in the range of 0.9466–0.9997 for the ILs used in this work. a is in the range of 42.17–87.65. The gradient b was set as a constant for all ILs in previous estimation model. However, b is in the range of −0.1717 to −0.0178 for the ILs analyzed in this work. Therefore, it is much more advisable to determine the gradient b based on the molecule structure. Thus the QSPR model is written as the following equation:

$$\sigma = \alpha + \beta T \quad (7)$$

$$\alpha = c + \sum \Psi_i \delta_i \quad (8)$$

$$\beta = d + \sum \Psi_j \delta_j \quad (9)$$

where δ is descriptor, and c, d, and ψ are parameters.

2.3. Topological index

TI is numerical quantity derived from a graph theoretical representation of the molecular structure through mathematical invariants. The *TI* used in this work was proposed on the base of atom characters (e.g. atom radius, atom electronegativity et al.) and atom positions in the hydrogen-suppressed molecule structure. Firstly, the molecule information is obtained and set in a total matrix (*TM*), which is generated from distance matrix D and character vector *CV*. D is used for determining the positions of non-hydrogen atoms in a molecule.

$$D = (d_{ij}), d_{ij} = \begin{cases} n & \text{if the path length between atom } i \text{ and } j \text{ is } n \\ 0 & \text{otherwise} \end{cases} \quad (10)$$

The *CV* is used for determining the characters of atoms in the hydrogen-suppressed molecule. Every atom in the hydrogen-suppressed graph is firstly numbered randomly with different numbers from 1 to N, which is the total number of non-hydrogen atom in the molecule. *CV* is defined as:

$$CV = (a_i)\ a_i \text{ is the elements that characterize the atom } i \quad (11)$$

To depict the molecule all-sidedly, eight *CV*s are defined using eight elements. And they are defined:

CV_1, a_i-$\pi \times$ van der Waal radii;
CV_2, a_i-atom weight;
CV_3, a_i-atom electronegativity;
CV_4, a_i-$\pi \times$ atom radius;
CV_5, a_i-exp (vertex degree, defined as the number of adjacent atoms);
CV_6, a_i-exp (fraction of hydrogen to atom i and hydrogens adjacent to it);
CV_7, a_i-exp(1/atom electronic shell number);
CV_8, a_i-exp(1/atom outermost electron number).
Another *CV* is defined as:
CV_9, a_i-0, which means no element.