



On the prediction of critical temperatures of ionic liquids: Model development and evaluation



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ARTICLE INFO

Article history:

Received 26 August 2015

Received in revised form

16 October 2015

Accepted 18 November 2015

Available online 23 November 2015

Keywords:

Critical temperature

T_c

Ionic liquid

Group contribution

GC

QSPR

Model

ABSTRACT

In this study, the Guggenheim equation was used to estimate the critical temperature (T_c) of 106 ionic liquids using experimental surface tension data as inputs. A group contribution (GC) and a Quantitative Structure-Property Relationship (QSPR) model were also developed to correlate/predict the T_c of ionic liquids. It was shown that a lack of sufficiently large database for T_c leads to the development of models with low prediction capability. The models output as well as the T_c values estimated from the surface tension data were compared with the critical temperatures calculated by the Valderrama et al. method. The results show that the Valderrama et al. method produces different data values compared with the values calculated by the Guggenheim equation. Neither the GC, QSPR, nor Valderrama's method is capable of reliable prediction of the T_c of ionic liquids. Consequently, the calculated T_c values are not reliable enough to be used in the development of corresponding state models for prediction of other thermophysical properties of ionic liquids. Any usage of critical properties of ionic liquids should be done with a serious caution.

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1. Introduction

Over the last few decades, researchers from around the world have undertaken numerous studies on ionic liquids (ILs) and demonstrated their potential use in various industrial applications. Ionic liquids are defined as molten salts which are generally liquid at or near room temperature (typically below 100 °C) due to the poor coordination of ions [1]. In general, they show unusual, but interesting properties such as extremely low saturation vapor pressure and negligible volatility, wide liquidus range, nonflammability, high thermal conductivity, and high physical and chemical stability [2]. These unique properties make them potential replacement solvents for conventional volatile and commonly toxic and flammable organic solvents in numerous industrial

applications such as extraction and separation processes [3–5], battery industry [6,7], solar panels [8,9], waste recycling [10,11], lubricants [12–15], fuel cells [16,17], polymer and biopolymer processing [18–20], electroplating [21,22], gas separation and CO₂ capturing [23–30], catalysis [31–33], and other processes [34–37].

In order to understand the behavior of ILs in such applications, thermodynamic models and property estimation methods are required. The critical properties, especially the critical temperature (T_c), are used commonly in the development of the corresponding state models. The critical temperature of a substance is the temperature at and above which vapor of the substance cannot be liquefied, no matter how much pressure is applied. The behavior of a fluid near its critical point is a specific property necessary to develop the thermodynamic models for fluids [38]. Due to presence of high electrostatic interactions and Coulombic forces, as well as short-range van der Waals interactions in ionic liquids, the critical properties of ionic liquids, cannot be measured as they are decomposed before their normal boiling temperature (T_b) are reached [39,40]. As a result, experimental data of critical properties of ILs as well as their T_b are not available in the literature and they can only be estimated in theory.

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Despite this limitation for the ionic liquids, some researchers have tried to use the available correlations and estimation methods of common organic compounds to estimate the critical properties of ILs. The most accepted approach is to use the relationship between critical temperature, density, and surface tension and thereafter, estimate the T_c of ionic liquids. According to the fact that the surface tension becomes zero at the critical temperature, two correlations were presented by Eötvös [41] and Guggenheim [42] which are shown in Equation (1) and Equation (2), respectively.

$$\gamma \left(\frac{M}{\rho} \right)^{2/3} = k(T_c - T) \quad (1)$$

$$\gamma = K(T_c - T)^{11/9} \quad (2)$$

where γ is surface tension, ρ is density, M is molar mass, k and K are two different constants. These equations usually can estimate the T_c of organic compounds pretty well; so it is assumed that they are applicable for ionic liquids too. This approach has been followed by the majority of researchers [38,40,43–47] to calculate and report the critical temperature of ionic liquids.

Another approach was followed by Valderrama et al. [39] where they used the Lydersen group contribution method to estimate the critical pressure and critical volume, and the Joback and Reid group contribution method to calculate the normal boiling temperature and the critical temperature of ionic liquids. They combined the best results of Lydersen's method with the best results of the Joback–Reid method to propose a “modified Lydersen–Joback–Reid” method and stated that this modified method had good results for molecules of high molecular weight. Thereafter, Valderrama *et al.* performed a consistency test and used a correlation for density to validate the estimated critical properties of ionic liquids. This correlation was developed earlier by Valderrama and Abu-Sharkh [48] to relate the critical properties of saturated liquids and petroleum fractions to their density. Consequently, they published the results of their calculations for 1130 ionic liquids [49].

Despite their interesting approach, there is unsatisfactory agreement between the values of T_c estimated by their method and the approach using Guggenheim equations for most of the ionic liquids. Nonetheless, these calculated critical properties were used by several researchers to develop corresponding state models for prediction of thermophysical properties of ionic liquids [50–56].

In this study, the available experimental data of surface tension of ionic liquids were used to estimate the critical temperature. Thereafter, a group contribution (GC) and a Quantitative Structure–Property Relationship (QSPR) models were developed to correlate/predict the T_c of ionic liquids. The results were compared with the values calculated by Valderrama et al. [49].

2. Model development methodology

2.1. Data preparation

The NIST Standard Reference Database #103b [58] and some newly published papers [59–63] were used to extract experimental data for surface tension of ionic liquids. In the next step, the data gathered were analyzed and screened to remove duplicates and outliers. As the surface tension is temperature dependent, data analysis was undertaken as follows:

- 1) Where there were several reported values of the desired property for a single temperature, the values were plotted against

temperature to find and remove the sources that their results had no agreement with others.

- 2) If there were only two sources, the values with the lowest uncertainty were incorporated into dataset utilized.
- 3) If the reported values had equal uncertainties, the latest published values were utilized.
- 4) To verify the potential outliers in the final dataset, the target values were plotted against temperature and a (non-)linear curve fitting algorithm was applied to fit the data. The data points which were “far” from the curve fitted were considered as outliers and omitted from the dataset.

The result of the screening process was 1513 data points for 139 ionic liquids constituted from 63 types of cations and 40 types of anions. Fig. 1 shows the number of ionic liquids in each family. In addition, the names and structures of cations and anions are available in Table S1 and Table S2 in the supplementary materials.

2.2. T_c calculation

As mentioned before, the most realistic value of critical temperature should be calculated from the Eötvös and/or Guggenheim equations. Previous studies [38,40] showed that the T_c calculated by these equations are in fair agreement with each other (less than 100 °C in most cases); however the Eötvös equation is more prone to deviations due to use of two sources of experimental data as inputs (surface tension and density). In addition, it is difficult to find experimental data for surface tension and density measured by the same laboratories at the same conditions. As a result, the Guggenheim equation was chosen for the estimation of critical temperature of ionic liquids. Unfortunately, for 33 ILs there was only one data point available and thus the T_c could not be calculated for them. Consequently, the critical temperature was calculated for 106 ionic liquids.

2.3. Model development

The GC and QSPR approaches were followed in the development of the models. The common approach in GC modeling is to use the linear summation of functional groups to develop a model. This approach is beneficial because of its simplicity, but its disadvantage is the weakness in the prediction of properties for compounds which exhibit complex behavior, have isomers, etc. [64–70]. The Quantitative Structure–Property Relationship is a well-established and highly respected technique to correlate diverse simple and

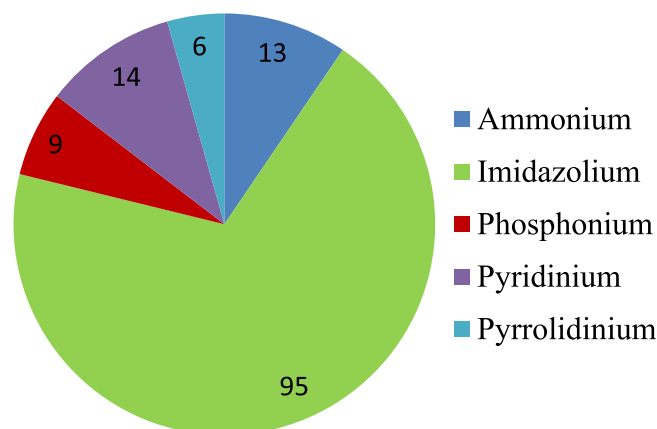


Fig. 1. The number of ionic liquids in different families used for modeling the critical temperature.

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