Journal of Molecular Liquids 216 (2016) 732–737

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

A simple method for prediction of density of ionic liquids through their molecular structure

Mohammad Hossein Keshavarz *, Hamid Reza Pouretedal, Ehsan Saberi

Department of Chemistry, Malek-ashtar University of Technology, Shahin-shahr, P.O. Box 83145/115, Islamic Republic of Iran

ARTICLE INFO

Article history:
Received 16 September 2015
Received in revised form 11 January 2016
Accepted 30 January 2016
Available online xxxx

Keywords:
Ionic liquid
Density
Correlation
Structural parameter

ABSTRACT

This paper introduces a reliable simple method to estimate density of a wide range of different types of ionic liquids. This method is based on two novel correlations in which the size, structure and type of cations and anions are essential parameters. The first correlation is derived from elemental composition, which is modified on the basis of correcting functions in the second one in order to consider inter ionic interactions and obtain more reliable results. For 249 different types of ionic liquids, where their calculated values with one of the best available methods were available, these correlations have been derived. The results of two simple correlations give good predictions as compared to the outputs of complex method. The new models have also been tested with experimental data of 235 new ionic liquids at atmospheric pressure and ambient temperatures that provide good predictions.

1. Introduction

Ionic liquids usually refer to room-temperature molten salts, which have been the subject of increasing attention because of their desirable physicochemical properties such as high thermal stability, large liquid range, high ionic conductivity, high solvating capacity, negligible vapor pressure, and non-flammability that make them ideal solvents for green chemistry [1,2]. Due to these appealing properties, ionic liquids are gaining wide recognition as potential replacements for conventional solvents in chemical processes [3–7]. Since they comprise at least one large and asymmetric organic cation or anion, their properties can be significantly tuned by appropriate modifications of the cation, anion, or both for a specific application [8–12].

Since density is crucial in the industrial process design involving ionic liquids, it is an important property among their physicochemical properties. It is desirable to have predictive models for calculating the ionic liquids properties as alternative to the experimental measurements because ionic liquids density data are either scarce and sometimes absent due to the large number of ionic liquids synthesized every year [13–28]. Furthermore, most of experimental standard test methods for measuring the density are time-consuming and expensive. However, it is important to have simple and reliable predictive methods for estimation density of a desirable new ionic liquid.

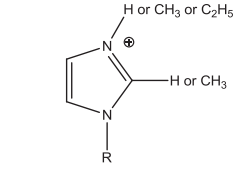
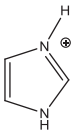
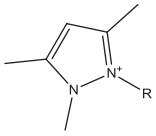
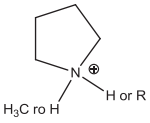
There are many Quantitative Structure–Activity Relationship (QSAR) or Quantitative Structure Property Relationship (QSPR) studies have been done in the past to predict the density of different classes of ionic liquids. Moreover, some studies have been done to investigate fast and reliable estimation of the molecular volume/molar volume/density of ionic liquids on the basis of group contributions. Some of these works related to the current study have been reviewed here. Rebelo et al. [29] provided an overview of phase behavior and thermodynamic properties of ionic liquids, ionic liquid mixtures, and ionic liquid solutions. Esperança and coauthors [30] studied on several phosphonium-based ionic liquids including trihexyltetradecylphosphonium chloride, trihexyltetradecylphosphonium acetate, and trihexyltetradecylphosphonium bis [31]-amide. They employed a simple ideal-volume model for estimation of densities of phosphonium-based ionic liquids at ambient conditions. Paduszynski and Domanska [32] have developed a method based on generalized empirical correlation and group contributions for prediction of density of pure ionic liquids over a wide range of temperature and pressure. Their model parameters include the contributions to molar volume for 177 functional groups as well as universal coefficients describing the P-ρ-T surface. Rebelo et al. [33] have accounted for the unique, doubly dual nature of ionic liquids through using a molecular perspective that emphasizes the doubly dual nature of ionic liquids underlying the existence of cations and anions forming high- and low-charge-density regions. Ye and Shreeve [34] developed volume parameters of some classes of ionic liquids for estimation of their densities at room-temperature. Gardas and Coutinho [35] improved group contribution method of Ye and Shreeve [34] for estimation of densities of ionic liquids in wide ranges of temperature and pressure. Jacquemin et al. [36] introduce a group contribution model for prediction of molar volumes and densities of several classes of ionic liquids as a function of temperature between (273 and 423) K at atmospheric pressure. Slattery and coworkers [37] described several simple relationships for estimation of the physical properties of some categories of ionic liquids from only their molecular volumes and an anion-dependent correlation. Palomar

* Corresponding author.
E-mail addresses: mhkeshavarz@mut-es.ac.ir, keshavarz7@gmail.com (M.H. Keshavarz).

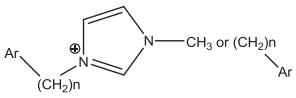
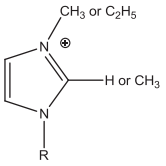
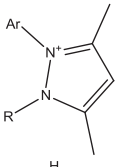
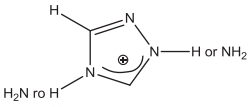
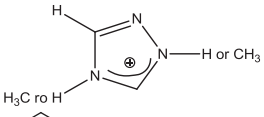
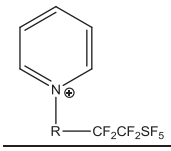
http://dx.doi.org/10.1016/j.molliq.2016.01.095
0167-7322/

Table 1
Summary of *DIL* and *IIL* molecular parameters.

Decreasing correcting function (DIL)

Cation	Anion	Condition	DIL
 R= alkyl group that may be contain -O- or -OH	Chloride, acetate, tricyanomethanide, dicyanamide, dicyanoazanide, nitrate, tetracyanoborate, tricyanomethane or perchlorate	Number of carbon atoms in alkyl group ≤ 3	1.0
		3 < number of carbon atoms in alkyl group ≤ 6 or alkyl group containing double bond	0.5
	Thiocyanate	Number of carbon atoms in alkyl group ≤ 3	0.4
		3 < number of carbon atoms in alkyl group ≤ 6	0.2
	Tetrafluoroborate	Number of carbon atoms in alkyl group ≤ 6	0.25
	Bis(oxalate)borate, bis(malonato)borate or dimethylphosphate	Number of carbon atoms in alkyl group ≤ 6	0.5
	Bis(trifluoromethylsulfonyl)imide or bis(pentafluoroethylsulfonyl)imide	Number of carbon atoms in alkyl group ≤ 6	0.3
	Bis(bis(pentafluoroethyl)phosphinyl)imide or bis(perfluorobutylsulfonyl)amide	Number of carbon atoms in alkyl group ≤6	1.3
		6 < number of carbon atoms in alkyl group < 18	0.8
	$RCOO^-$	Number of carbon atoms in alkyl group ≤ 6	0.8
		6 < number of carbon atoms in alkyl group ≤ 9	0.6
	Bis(trifluoromethylsulfonyl)amide	Number of carbon atoms in alkyl group ≤ 4	1.8
	Trifluoroacetate, hexanoate, dicyanoamide, bis(trifluoromethylsulfonyl)imide, formate, nitrate or (fluorosulfonyl)(5-I-3-oxa-octafluoropentanesulfonyl)imide	Number of carbon atoms in alkyl group ≤ 6	0.8

Increasing correcting function (*IIL*)

Cation	Anion	Condition	IIL
	Chloride, trifluoroacetate, imidazolate, propionate or bis(trifluoromethanesulfonyl)imide	–	0.4
	Hexafluorophosphate, dicyanoamide, thiocyanate or saccharine	–	1.1
	Methylsulphate, bis(salicylate)borate or bis(2,2,2-trifluoroethoxysulfonyl)imide	Number of carbon atoms in alkyl group ≤ 4	1.4
	Glutamate, tosylate or trifluoromethanesulfonate	Number of carbon atoms in alkyl group > 4	0.6
	Hexafluorophosphate	Number of carbon atoms in alkyl group ≤ 10	0.2
		Number of carbon atoms in alkyl group ≤ 10 or alkyl group containing amino group	0.7
	Thiocyanate or bis(trifluoromethylsulfonyl)imide	Number of carbon atoms in alkyl group ≥ 10 or alkyl group containing $SF_5CF_2CF_2$- group	0.8
	Methanesulfonate or tetrafluoroborate	–	0.8
	Nitrate or perchlorate	–	0.8
	4,5-Dinitroimidazolate	–	0.7
	Bis(trifluoromethylsulfonyl)imide	Number of carbon atoms in alkyl group ≤ 4	0.8

and coworkers [12] used COSMO-RS software to determine the density of 40 imidazolium salts. They have also applied COSMO-RS and artificial neural network (ANN) to predict density of 45 imidazolium-based ionic liquids [38]. Trohalaki et al. [39] derived QSPR model to predict the density of 13 of triazolium bromides using CODESSA software through employing electrostatic, quantum mechanical and thermodynamic descriptors. Valderrama et al. [40] used ANN and group contribution method (GCM) to estimate the density of 103 of ionic liquids. Lazzus [41] used