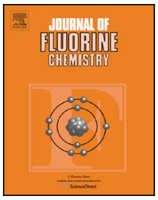
Journal of Fluorine Chemistry 186 (2016) 19–27

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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



A group contribution model for prediction of the viscosity with temperature dependency for fluorine-containing ionic liquids

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ARTICLE INFO

Article history:
Received 5 October 2015
Received in revised form 31 March 2016
Accepted 2 April 2016
Available online 9 April 2016

Keywords:
Group contribution
GC
Viscosity
Fluorine
Ionic liquid

ABSTRACT

One of the barriers against application of ionic liquids (ILs) for industrial separations is their relatively high viscosity. The viscosity of the IL can however be decreased by inserting the fluorinated moieties into the anion structure. Hence, if one could find a relationship between chemical structure, temperature, and viscosity one could design fluorine-containing ILs (F-ILs) with desired specifications. In this communication, two extensive dataset of F-ILs were gathered; one with reliable sources consisting of 863 experimental viscosities for 85 F-ILs, and the other including unreliable sources consisting of 1160 experimental data points for 332 F-ILs. Using the reliable dataset an efficient group contribution (GC) model was developed, which employs a total of 35 functional groups to estimate the temperature-dependent viscosities of F-ILs. The proposed GC model produced a low average absolute relative deviation (AARD) of 3.23%, root-mean-square error (RMSE) of 0.19, and coefficient of determination (R^2) of 0.977. The other model developed using the second database only parameterized in supplementary materials.

1. Introduction

Over the last few decades, numerous studies have been undertaken on ionic liquids (ILs) and their potential use in various industrial applications has been demonstrated by several researchers. Their generally low melting point of below 100 °C is one of the most important properties of ILs, which are often hydrolytically stable. Ionic liquids are typically composed of a large organic cation and an anion of inorganic or organic compounds and are generally liquid at or near room temperature (typically below 100 °C) [1–4].

Generally, ionic liquids have some significant properties compared with common organic solvents such as higher thermal stability, extremely lower vapor pressures and thus negligible volatility, which make them desirable as potential solvents [3,5–7]. Due to these properties, ILs have numerous potential applications, such as in extraction and separation processes [8–10], lubricants [11–14], waste recycling [15–18], catalysis [19,20], gas separation and CO_2 capturing [21–25], and many more [26–33].

One of the barriers against replacing commonly used solvents with ionic liquids in various applications is the relatively high viscosity (η) of ILs which results in low diffusion coefficients, slow mass transfer, and low electrical conductivity [34,35]. Therefore, research has to be undertaken to synthesize ILs with low viscosity and low melting points. Initial investigations have shown that the insertion of fluorinated moieties into the molecular structure of ionic liquids could result in reduction of viscosity as well as the melting point of ILs [2,34,36–38].

ILs consist of ions, viz. a cation and an anion. In theory the cation and anion can be selected to have molecules with desired properties for a particular application. As such, ILs have been termed as “tunable” and “designable” materials [39]. Consequently, the values of viscosity can be tuned by selecting appropriate combinations of ions, especially fluorine-containing ions. The process of selection can be sped up by using a predictive model which has the ability to correlate the viscosity data based on chemical structure of ions or other thermophysical properties.

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http://dx.doi.org/10.1016/j.jfluchem.2016.04.001
0022-1139/

Table 1
Summary of different models for predicting the ln(η) of ILs.

Model	Model Type and parameters	N_{ILs}	N_{data}	AARD %	Comments
Abbott [40]	Correlation	11	n.a.	122	10 ILs contained fluorine atom.
Bandres et al. [41]	Correlation	8	n.a.	4.5	7 ILs contained fluorine atom.
Eiden et al. [46]	Correlation, 3 parameters (Quantum Mechanics)	155	810	n.a.	122 ILs contained fluorine atom. RMSE is 0.26 for external validation dataset (83 ILs with 145 data points)
Gardas and Coutinho [49]	GC, 13 parameters, ρ	30	500	7.78*	Only 19 ILs contained fluorine atom. *AARD% is in linear scale.
Gardas and Coutinho [52]	GC, 12 parameters	25	482	7.50*	Only 16 ILs contained fluorine atom. *AARD% is in linear scale.
Tochigi and Yamomoto [55]	QSPR, 24 parameters	161	334	5.04	149 ILs contained fluorine atom. Most of the ILs had just one data point.
Bini et al. [56]	QSPR, 4 parameters.	33	66	n.a.	Authors proposed two models for T = 293 K and T = 353 K.
Gharagheizi et al. [57]	GC, 47 parameters	443	1672	6.32	638 duplicated data points were used. By removing the duplicates, the AD% was risen to 7.1%. 724 data points were for F-ILs
Valderrama et al. [58]	ANN	58	327	n.a.	
Billard *et al.* [59]	ANN	99	99	10	The data were only at 298 K.
GC Model (1)	GC, 35 parameters	85	863	3.23	The reliable data sources were used.
GC Model (2)	GC, 36 parameters	332	1160	4.85	The entire database including unreliable data sources was used.

Abbott [40] recommended the application of hole theory for the definition of the viscosity of ILs and molecular liquids. Despite the introduction of this theory for the estimation of viscosity, the model did not produce satisfactory predictions for ILs and had a percentage average absolute relative deviation (AARD%) of 122%. Bandres et al. [41] predicted the viscosity of 8 pyridinium ionic liquids by modifying the hole theory suggested by Abbott [40]. They introduced an efficient IL radius (R^*) to improve the estimations. The R^* was fitted to real/laboratory viscosity data points at a pressure of 0.1 MPa. Consequently, their method yielded an AARD% of 4.5%. The weakness of their model was its lack of predictive capability for ILs without any experimental data, as the model needed experimental data to evaluate R^*.

In a different approach, Krossing and Slattery [42] concluded that viscosity increased exponentially with increasing the molecular volume (V_m). It was found that the relationship between viscosity and molecular volume was independent of the cation structure for a large range of common cations. However, it was highly anion dependent thus two coefficients should be calculated for each anion and they are valid for a limited range of temperature (i.e. 20–22 °C) [43]. Moreover functionalized cations are required their own pair of coefficients. As a result, cation and anion specific coefficients as well V_m should be available for prediction of viscosity. These limitations hurt the applicability of this approach, especially for the prediction of viscosity of ionic liquids before synthesis which the coefficients are not available. V_m is another property which should be measured by experiments or by application of Equation of State (EOS) theories [42–45].

To overcome the limitations of previous method, Eiden et al. [46] presented a novel approach and proposed a new temperature-dependent correlation without further input of any experimental data. For the viscosity, the inputs are only some basic physical observables like the Gibbs solvation energy which was calculated using Quantum Mechanics at the DFT-level (RI-)BP86/TZVP/COSMO, the molecular radius, calculated from the molecular volume V_m of the ion volumes, and the symmetry number (σ), according to group theory. The model was tested with some success on 83 ILs (9 different cations and 11 anions) with a RMSE of 0.26. Despite the apparent simplicity of the correlation, complicated Quantum Mechanics calculations have to be performed using special software like Gaussian [47] and Cosmotherm.

In another study, Bulut et al. [48] investigated the temperature dependence of the viscosity of mildly functionalized and non-functionalized $[Tf2N]^-$ ionic liquids. They used Arrhenius, Litovitz, and Vogel–Fulcher–Tammann (VFT) equations as well as the molecular volume (V_m) to fit the experimental viscosity data. They found that VFT equation had the best fit, but it needed an empirical fitting parameter T_0. This parameter can be estimated if the glass transition temperature (T_g) of the ionic liquid is known, otherwise the VFT equation is not applicable for prediction of the viscosity of ionic liquids with unknown value of T_g.

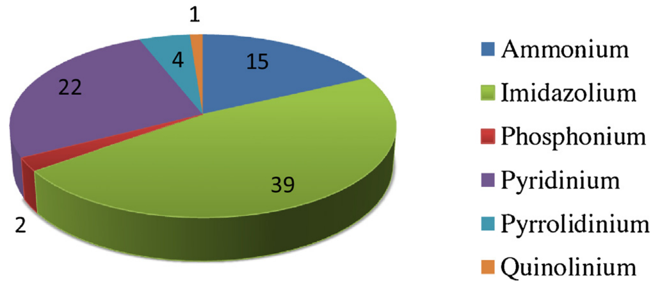

Fig. 1. The number of ionic liquids in different families used to model the viscosity (refined dataset).

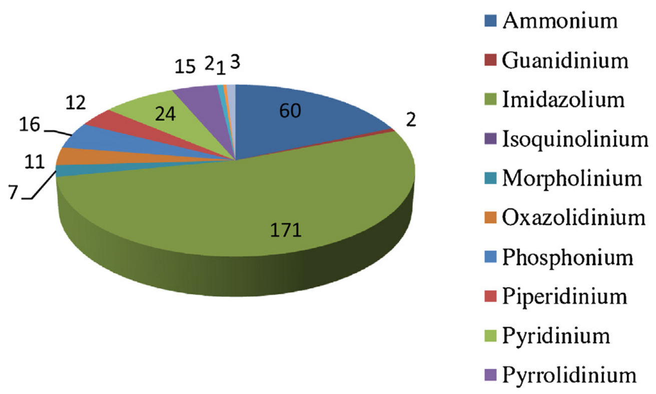

Fig. 2. The number of ionic liquids in different families used to model the viscosity (unreliable dataset).