



Review

A review on the transport properties of ionic liquids

Xiaojing Wang^a, Yanling Chi^b, Tiancheng Mu^{c,*}^a School of Science, Beijing University of Civil Engineering and Architecture, Beijing 100044, China^b Materials Science and Engineering College, Northeast Forestry University, Harbin 415000, China^c Department of Chemistry, Renmin University of China, Beijing 100872, China

ARTICLE INFO

Article history:

Received 5 November 2013

Received in revised form 27 December 2013

Accepted 7 March 2014

Available online 20 March 2014

Keywords:

Transport property

Ionic liquid

Correlation

Molecular dynamics simulation

ABSTRACT

Transport properties include the thermal conductivity for heat transfer, the viscosity for the momentum transfer, and the diffusion coefficient for mass transfer. The transport properties are very important for chemical engineering design. The ionic liquids are liquids with good conductivity thus may have promising applications in battery industry. However, the high viscosity hinders the applications of them. In this paper, we firstly reviewed the values of transport properties of pure ionic liquids, then these properties of the mixtures of ionic liquids with other compounds were discussed, and lastly we reviewed the correlation researches on the transport properties of systems including ionic liquids and the molecular dynamics simulation investigations on these systems.

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1. Introduction

Ionic liquids (ILs) have attracted much attention in the scientific community recently due to their novel and highly customizable properties [1,2]. They have been used in various fields such as extraction and separation [3,4], catalyst, materials fabrication [5,6], analytical technology, and energy [7]. The transport properties include the diffusion rate coefficients such as the thermal conductivity (for heat transfer) [8–11], the viscosity (for momentum transfer), and diffusion coefficient (for mass transfer) [12–15]. Thus, the transport properties play crucial roles in chemical and engineering processes. The relatively high viscosity of ILs poses serious limitations to the use of ILs. Considered the high

viscosity of most ILs, the transport properties of ILs are more important. Since the ILs are composed of cations and anions, the electric conductivity of ILs is widely concerned [16–19]. According to the previous reports, the transport properties of ILs are mainly determined by hydrogen bonding, van der Waals forces, molecular weight and mobility [16,20]. There have been several reviews published on the transport properties, and different models (correlation, group contribution [21], quantitative structure property relationship (QSPR) [22], computer-aided molecular design [23], etc.) for the prediction of the transport properties of ILs were compared.

Hence, in this mini-review, we mainly discuss the viscosities of ILs. Both the experimental data and prediction methods were discussed. The transport properties of pure ILs, the mixtures of ILs with molecular solvents, or the mixtures of two or more ILs were discussed. The definition and nomenclature of mixtures of ILs were given in a previous report

* Corresponding author. Tel.: +86 10 62514925; fax: +86 10 62516444.
E-mail address: tcmu@chem.ruc.edu.cn (T. Mu).

[24]; in that report, they also gave a comprehensive review of the properties of mixtures of ionic liquids. For prediction methods, Das and Roy have given a comprehensive review on the QSPR models [22]. Therefore we will only discuss the correlation methods based on group contribution concept because it is simple and easy to use, and molecular dynamics because it is molecular based.

2. Transport properties of pure ionic liquids

The transport properties of ILs are determined by the nature of its cation and anion and conditions such as temperature and pressure. Tokuda et al. investigated the influence of cation, anion, the alkyl chain length of cation, and temperature on the transport properties of IL [25–28].

The transport properties (diffusion coefficient, viscosity, ionic conductivity) of ILs: (1) with a variety of fluorinated anions combined with [BMIM] [27]; (2) with different cationic structures [BMIM], [BPy], [BMPyrr], and [(n-C₄H₉)(CH₃)₃N] combined with an anion, [Tf₂N] [26]; (3) with imidazolium based cation but different alkyl chain length ([C_nMIM][Tf₂N], n = 1, 2, 4, 6, and 8) [28]; were measured and correlated with Vogel–Fulcher–Tamman (VFT) equation (Eqs. (1)–(3)), the viscosity and ionic conductivity results are presented in Tables 1 and 2, respectively.

$$D = D_0 \exp \left[-B_1 / (T - T_{0,1}) \right] \quad (1)$$

$$\eta = \eta_0 \exp \left[B_2 / (T - T_{0,2}) \right] \quad (2)$$

$$\sigma = \sigma_0 \exp \left[-B_3 / (T - T_{0,3}) \right] \quad (3)$$

The anionic effect on the self-diffusion coefficients of the cation and anion, viscosity, and ionic conductivity of ILs [BMIM] with a variety of fluorinated anions at 30 °C lead to the following conclusions: (1) The VFT equation is suitable to describe the temperature dependencies of the transport properties such as self-diffusion coefficient, viscosity, ionic conductivity, and molar conductivity; (2) the self-diffusion coefficients exhibit higher values for the cation compared with the anion, even if its radius is larger than that of the anionic radii. The cationic and anionic diffusion coefficients for the ILs follow the order: [BMIM][Tf₂N] > [BMIM][TFA] > [BMIM][OTF] > [BMIM][BF₄] > [BMIM][BETI] > [BMIM][PF₆]. The order of the diffusion coefficients greatly contrasts to the viscosity data; (3) the ratio of the experimental molar conductivity to that of the calculated data follows the order: [BMIM][PF₆] > [BMIM][BF₄] > [BMIM][BETI] > [BMIM][Tf₂N] > [BMIM][OTF] > [BMIM][TFA] [27].

Table 1

VFT parameters of viscosity data for [BMIM]-based [27], [C_nMIM][Tf₂N] [28] and [Tf₂N]-based [26] ILs.

IL	$\eta_0/10^{-1}$ mPa s	B/10 ² K	T ₀ /K
[BMIM][BETI]	1.7 ± 0.2	7.63 ± 0.38	180 ± 3
[BMIM][Tf ₂ N]	2.5 ± 0.2	6.25 ± 0.22	180 ± 2
[BMIM][OTF]	3.7 ± 0.6	5.70 ± 0.37	193 ± 4
[BMIM][PF ₆]	3.6 ± 0.5	6.39 ± 0.25	201 ± 2
[BMIM][TFA]	1.1 ± 0.2	7.88 ± 0.53	177 ± 4
[BMIM][BF ₄]	2.1 ± 0.1	6.97 ± 0.69	185 ± 6
[MMIM][Tf ₂ N]	2.9 ± 0.6	5.87 ± 0.57	178 ± 7
[EMIM][Tf ₂ N]	4.0 ± 1.3	5.09 ± 0.81	182 ± 10
[HMIM][Tf ₂ N]	1.6 ± 0.2	7.57 ± 0.39	173 ± 3
[OMIM][Tf ₂ N]	1.5 ± 0.2	8.02 ± 0.30	173 ± 2
[BPy][Tf ₂ N]	2.1 ± 0.4	6.71 ± 0.52	179 ± 5
[BMPyrr][Tf ₂ N]	2.9 ± 0.4	6.51 ± 0.31	181 ± 3
[(n-C ₄ H ₉)(CH ₃) ₃ N][Tf ₂ N]	4.5 ± 0.6	5.34 ± 0.27	199 ± 3

Table 2

VFT parameters of ionic conductivity data for [BMIM]-based [27], [C_nMIM][Tf₂N] [28] and [Tf₂N]-based [26] ILs.

IL	$\sigma_0/10^{-1}$ S cm ⁻¹	B/10 ² K	T ₀ /K
[BMIM][BETI]	7.1 ± 0.5	7.96 ± 0.22	169 ± 2
[BMIM][Tf ₂ N]	4.3 ± 0.2	5.65 ± 0.14	178 ± 2
[BMIM][OTF]	9.8 ± 0.8	7.93 ± 0.26	162 ± 3
[BMIM][PF ₆]	14.7 ± 1.0	8.55 ± 0.20	174 ± 2
[BMIM][TFA]	9.2 ± 0.4	7.19 ± 0.13	172 ± 1
[BMIM][BF ₄]	13.8 ± 0.6	7.41 ± 0.13	174 ± 1
[MMIM][Tf ₂ N]	6.6 ± 0.4	5.62 ± 0.18	168 ± 3
[EMIM][Tf ₂ N]	5.8 ± 0.2	5.54 ± 0.13	165 ± 2
[HMIM][Tf ₂ N]	6.1 ± 0.3	7.31 ± 0.13	168 ± 1
[OMIM][Tf ₂ N]	6.1 ± 0.2	8.11 ± 0.12	166 ± 1
[BPy][Tf ₂ N]	5.5 ± 0.5	6.33 ± 0.24	175 ± 3
[BMPyrr][Tf ₂ N]	5.6 ± 0.2	6.75 ± 0.14	171 ± 1
[(n-C ₄ H ₉)(CH ₃) ₃ N][Tf ₂ N]	6.1 ± 0.1	6.89 ± 0.04	177 ± 0

To the ILs with different type of cations, the magnitude of cationic and anionic diffusion coefficients for the ILs follows the order: [BMIM][Tf₂N] > [BPy][Tf₂N] > [BMPyrr][Tf₂N] > [(n-C₄H₉)(CH₃)₃N][Tf₂N]; which coincides with the reverse order to the viscosity data. The ratio of the experimental to that of the calculated molar conductivity data from the ionic diffusivity using the Nernst–Einstein equation follows the order: [BMPyrr][Tf₂N] > [(n-C₄H₉)(CH₃)₃N][Tf₂N] > [BPy][Tf₂N] > [BMIM][Tf₂N] at 30 °C, which also provides quantitative information on the active ions contribution to ionic conduction [26].

The investigation of the ILs with imidazolium based cation but different alkyl chain length led to the following conclusions. The summation of the cationic and anionic diffusion coefficients follows the order: [EMIM][Tf₂N] > [MMIM][Tf₂N] > [BMIM][Tf₂N] > [HMIM][Tf₂N] > [OMIM][Tf₂N]. The ratio of the calculated and experimental data of molar conductivity decreases with increasing number of carbon atoms in the alkyl chain [28]. The effect of position and length of alkyl substituent in pyridinium based ILs has been studied too. It was found that the position of the methyl substituent had significant influence of on the transport properties. Walden plots indicate that these ILs have high ionicity, closer to the “ideal” KCl line, suggesting less ion association compared to their 1-butyl-3,5-dimethylpyridinium homologues [29]. The temperature dependence of transport properties of ammonium-based ILs N-alkyl-triethylammonium [Tf₂N] with different alkyl chain length on the cation (from 293.15 to 363.15) K [30] and dynamic viscosity for three phosphonium-based ionic liquids: tributyl methyl phosphonium methylsulfate (P₄₄₄₁C₁SO₄), tributyl ethyl phosphonium diethylphosphate (P₄₄₄₂(C₂)₂PO₄) and tributyl octyl phosphonium chloride (P₄₄₄₈Cl) (from 293.15 to 343.15 K) can be described by VFT equations.

The high-pressure (up to 126 MPa) viscosity of [EMIM], [HMIM], and [DMIM] with [Tf₂N], and [HMIM] with [Tf₂N], [PF₆], and [BF₄] was measured. The increase of the alkyl-chain length induced the viscosity increase at elevated pressures. [HMIM][PF₆] and [BMIM][PF₆] demonstrated a nonlinear pressure dependence even at relatively moderate pressures (to 30 MPa) [31]. Harris et al. carried out a series of research on the temperature and pressure dependence of viscosity of ILs [32–37]. The transport properties of pyridinium based ILs [29], pyrrolidinium based ILs [38], phosphonium-based ILs [39,40] could be well described with the VFT equation.

3. Transport properties of the mixtures including ionic liquids

A considerable amount of work on the transport properties of pure IL has been published. At the same time, the properties of both mixtures of IL with molecular solvent and the mixtures of two or more ILs are important because the mixtures might enormously enlarge the applications of the ILs.

Seddon et al. discovered that the viscosity of ionic liquid mixtures with impurities or additives was dependent mainly on the mole fraction

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