

## A Group Contribution Method for the Correlation of Static Dielectric Constant of Ionic Liquids\*

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**Abstract** Static dielectric constant is a key parameter to estimate the electro-viscous effect which plays important roles in the flow and convective heat transfer of fluids with ions in microfluidic devices such as micro reactors and heat exchangers. A group contribution method based on 27 groups is developed for the correlation of static dielectric constant of ionic liquids in this paper. The ionic liquids considered include imidazolium, pyridinium, pyrrolidinium, alkylammonium, alkylsulfonium, morpholinium and piperidinium cations and various anions. The data collected cover the temperature ranges of 278.15–343.15 K and static dielectric constant ranges of 9.4–85.6. The results of the method show a satisfactory agreement with the literature data with an average absolute relative deviation of 7.41%, which is generally of the same order of the experimental data accuracy. The method proposed in this paper provides a simple but reliable approach for the prediction of static dielectric constant of ionic liquids at different temperatures.

**Keywords** ionic liquid, static dielectric constant, group contribution method

### 1 INTRODUCTION

Ionic liquids are molten salts that are liquid at or near room temperature with specific organic cations and organic or inorganic anions [1]. They have received an increasing amount of interest due to their unique characteristics, *i.e.*, negligible vapor pressure at normal temperature and pressure, wide liquidus ranges, tunable physicochemical properties and high solvating capacity for both organic and inorganic compounds. Ionic liquids have emerged as a promising class of solvents for a wide variety of applications including organic synthesis, extraction separation, biocatalysis, material preparation, electrochemistry as well as heat transfer and heat storage fluid, and so on [2–7]. Most efforts in ionic liquids have been focused on the investigation of their potential applications, the preparation of novel ionic liquids, and measurement of basic physical properties of ionic liquids, while the characterization of the structure-property relationship of ionic liquids that is equally important has been lagged behind. The experimental data available are mainly for melting point, density, viscosity, electrical conductivity and surface tension, while few efforts have been paid to the determination of polarity of ionic liquids, especially the static dielectric constant of ionic liquids.

Static dielectric constant represents the polarity and solvating capability of liquids, and it is an important input parameter in many solvation simulation processes [8]. Moreover, it is crucial in the study of flow and convective heat transfer of fluids with ions in micro devices, because when fluids with ions flow in micro devices, such as micro pumps, micro reactors

and micro heat exchangers, the electro-viscous effect exists, which will greatly influence the flow characteristics and heat transfer of fluids [9–11]. The flows of incompressible Newtonian liquids incorporating electro-viscous effect through a circular tube are governed by the Poisson equation relating the electrical potential to the charge distribution and the Navier-Stokes equation with an electrical body force term, as described by Eqs. (1) and (2) in dimensionless form [11]:

$$\nabla^2 U = -\frac{1}{2} K^2 (n_+ + n_-) \quad (1)$$

$$\frac{\partial \mathbf{V}}{\partial t} + \nabla \cdot (\mathbf{V}\mathbf{V}) = -\nabla P + \frac{1}{Re} \nabla \cdot [\nabla \mathbf{V} + (\nabla \mathbf{V})^T] - \frac{BK^2}{Re^2} (n_+ - n_-) \nabla U \quad (2)$$

$$B = \frac{\rho k_b^2 T^2 \varepsilon_0 \varepsilon}{2z^2 e^2 \eta^2}, \quad K = \sqrt{\frac{2z^2 e^2 n_0 R^2}{\varepsilon_0 \varepsilon k_b T}} \quad (3)$$

$\varepsilon$  and  $\varepsilon_0$  are the static dielectric constant of the fluid and vacuum permittivity, respectively.  $t$ ,  $K$ ,  $B$ ,  $\rho$ ,  $\eta$ ,  $k_b$ ,  $e$ ,  $z$ ,  $R$ ,  $T$ ,  $n_0$ ,  $P$ ,  $Re$ ,  $\mathbf{V}$ ,  $U$ ,  $n_+$  and  $n_-$  are the time, dimensionless electro-kinetic parameter, dimensionless physical property parameter, density, viscosity, the Boltzmann constant, elementary charge, valence of the ion, radius of the tube, temperature, bulk ionic number per unit volume, pressure, Reynolds number, velocity, electrical potential, the number of cations per unit volume and the number of anions per unit volume, respectively. The last term in the right side of Eq. (2) represents an electrical body force due to electro-viscous

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effect. From the above equations, it is obvious that the static dielectric constant of fluid is a key parameter in the calculation of additional drag caused by this electro-viscous effect. Since ionic liquids are entirely composed of ions, the electro-viscous effect may exist when ionic liquid flows in micro channels, and the above three equations may still hold for the flow of ionic liquid in micro channels. Therefore, it is a must to get the static dielectric constant of ionic liquid to study the flow characteristics and convective heat transfer of ionic liquid in micro channels, which will be important for the design and optimization of the above mentioned micro chemical equipment. Despite of its significant importance in chemical industry, the static dielectric constant of many ionic liquids is not known to date. Conventional capacitance method fails for static dielectric constant measurement of ionic liquids due to the short-circuited sample cell by the electrical conductance of ionic liquids. The main method for ionic liquid static dielectric constant measurement is microwave dielectric relaxation spectroscopy (DRS) [12], which demands expensive device and sophisticated data processing. Furthermore, there are approximately  $10^{18}$  combinations of ions that could lead to useful ionic liquids [13], and it is impossible to measure the static dielectric constant of all ionic liquids experimentally. Development of simple and rapid methods for the estimation of the static dielectric constant of ionic liquids is important, which will be helpful for the design of task-specific ionic liquids and speed up their industrial applications.

Several studies have been reported for the estimation of the static dielectric constant of ionic liquids. By combining volume-based thermodynamics (VBT) and quantum chemical calculations, Krossing *et al.* [14] have proposed a method for the estimation of static dielectric constant ( $\epsilon$ ) of ionic liquids. The prediction mainly depends on the Gibbs solvation energy and the molecular volume of the ions. This method requires the knowledge of quantum chemical calculations and it assumes that Gibbs solvation energy is independent of temperature, which is not true for most liquids, and reduces the accuracy of the method. Ludwig *et al.* [15] have attempted to predict  $\epsilon$  by Fourier transform infrared spectroscopy (FTIR) based on the association of water molecules in ionic liquids and makes use of shifts in the stretching frequencies of water molecules. Ludwig's method is limited to the ionic liquids that do not hydrolyze upon contact with water and also limited by the assumption that ionic liquid solutions are homogeneous fluid. Studies have indicated that many ionic liquids are nano-structured materials and will segregate into polar and nonpolar regions with the addition of water [16–18]. Singh *et al.* [19] predicted  $\epsilon$  by means of the ratio of internal pressure and cohesive energy density. This method shows reasonable accuracy for ionic liquids with anions  $\text{Cl}^-$ ,  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{NTf}_2]^-$  and  $[\text{CF}_3\text{SO}_3]^-$ , while ionic liquids having anions alkylsulfate tend to have a large deviation up to 60%. Furthermore, some physical properties which are not easy to obtain, such as heat of vaporization, are

required for the determination of static dielectric constant in Singh's method, which restricts its applications.

In this paper, a simple correlation method for the correlation of the static dielectric constant of ionic liquids with a group contribution method based on 27 groups is proposed. The method developed in this work overcomes the limitations of the previously existing methods and it has a better correlation accuracy and wider application ranges for the prediction of the static dielectric constant of ionic liquids.

## 2 MODEL DEVELOPMENT

Static dielectric constant is defined as the zero frequency limit of the complex permittivity in the absence of ionic conductivity, and it reflects the contributions from molecular polarization (ionic polarization and electronic polarization) and the orientation polarization caused by the permanent dipole moment of the molecule [20]. A general relationship between the static dielectric constant  $\epsilon$  and the microscopic properties, such as molecular polarizability  $\alpha$ , is given by Böttcher theory [21]:

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi N_A \rho}{M[1 - f(a)\alpha_s]} \left[ \alpha + \frac{1}{3kT} \frac{\mu^2}{1 - f(a)\alpha_s} \right] \quad (4)$$

$N_A$  is Avogadro's number,  $\mu$  is permanent dipole moment,  $M$  is the molecular mass and  $\alpha_s$  is the sum of all forms of molecular polarizability which represents the deformability of the molecule and ions in an external electrical field, and it is made up of electronic polarizability and ionic polarizability. Further,  $f(a)$  is the static reaction field factor that depends on the cavity radius,  $a$ , and it is expressed as  $f(a) = 2(\epsilon - 1)/[a^3(2\epsilon + 1)]$ . The first and second term in the parenthesis in the right side of Eq. (4) represent the contribution of molecular polarization and the orientation polarization caused by the permanent dipole moment of the molecule to static dielectric constant, respectively.

Ionic liquids are highly structured and their microscopic behavior is dominated by strong, long-ranged inter-ion Coulomb interactions [22]. The study of Izgorodina's group [20] has indicated that ionic polarization contributes significantly to the static dielectric constant of ionic liquids, and they also pointed out that the static dielectric constant of ionic liquids may not be mainly influenced by the size of the permanent dipole moment, indicating that the contribution of orientation polarization caused by the permanent dipole moment of the ions to static dielectric constant of ionic liquids may not be significant. Therefore, for ionic liquids, it might be reasonable for us to assume that the second term in the parenthesis in the right side of Eq. (4), which reflects the contribution of orientation polarization caused by the permanent dipole moment to static dielectric constant, can be neglected. Using the Onsager approximation [21],  $4\pi N_A \rho a^3 / (3M) = 1$ , for the cavity radius and neglecting the contribution of

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