

# Assessment of Stokes-Einstein Equation in Combination of the Hole Theory for Estimating the Transport Properties of Ionic Liquid

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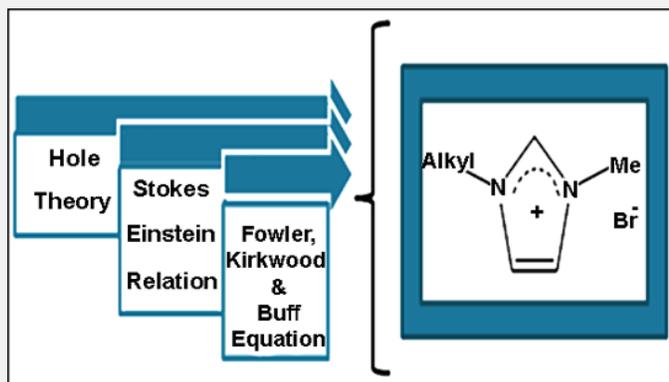
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## ABSTRACT

In this paper, the validity of the Stokes-Einstein (SE) equation for estimating the transport properties (e.g. viscosity) of imidazolium-based ionic liquids [C<sub>n</sub>mim]Br (n=2,4,5,6) was examined. To achieve this goal, the “hole theory” has been utilized for estimating the mean radius of the hole. According to the hole theory formalism, the mean radius of the hole is related to surface tension. To do so, the Fowler recipe of the Kirkwood-Buff (FKB) equation has implemented the calculation of Lennard-Jones's contribution to the surface tension of ILs. In the following, an assessment of the SE equation is depicted by drawing of  $\frac{D \times \eta}{T}$

versus  $\frac{1}{r}$ . Our test confirms the linearity of the diagram and then verifies the validity of the aforementioned approach. The results show that within the imidazolium family, as the cation alkyl chain length increases due to the increased Coulombic forces between the cation and the anion, surface tension decreases.



**Keywords:** Ionic liquids, Stokes-Einstein equation, hole theory, transport properties, radius of ions

## 1. Introduction

Ionic Liquids (ILs) as novel fluids have attracted great interest during the last few years [1]. Generally, ILs are a class of organic salt, which consists of organic cations and usually inorganic anions where one or both the ions are large, and the cation has a low degree of symmetry [2]. The physicochemical properties of the IL are mostly determined by the nature of the cation and or anion [3]. To optimize the use of ILs, especially in industrial applications, and design the new desirable ILs, a fundamental understanding of the physicochemical properties of ILs is very important [4]. ILs have extremely useful properties such as no detectable vapor pressure, wide liquidized range, high ionic conductivity [5], excellent thermal and chemical stability, and non-flammability [6].

ILs are being investigated for a variety of applications including extraction [7], separation [8], designable solvents for a variety of processes such as catalysis and organic synthesis, lithium batteries, fuel cells, super-capacitors, solar cells, material sciences, and engineering [9]. Thermophysical properties of fluids play fundamental roles in many diverse areas of science and engineering. They are divided into two categories: transport properties and equilibrium properties [10-15]. Indeed, the structural properties of ILs have received conspicuous attention [16-18] alongside both transport and equilibrium properties.

Among the equilibrium properties ‘surface tension’ has great importance [11, 12]. Surface tension has the main role in distillation, absorption, separation, and extraction [19]. Knowledge of the surface tension properties and their relationship to the chemical structure of ILs [16-17] is essential to selecting the right IL, for a particular application

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[20-21]. Despite the growing importance of ILs, the amounts of available correct experimental data on their transport properties of them are rare. The experimental data on surface tension for ILs reported in the literature are scarce and often conflicting; therefore, it is required to develop theoretical studies using correlation and predictive methods [7].

To do so, a microscopic understanding of the properties of ILs at a molecular level is necessary [22]. Therefore, we have a brief discussion on the theoretical models because they are simple and easy to use, and can greatly aid in predicting the properties and performance of ILs. Up to the authors' knowledge, there is no clear understanding regarding the prediction of the transport properties of ILs and different ionic structures by the SE equation. The hole theory (HT) is the most commonly used model for the investigation of ion movement in ILs at high temperatures [5]. Henceforth, the HT would need to consider the creation of holes within the fluid mixture instead. The aforesaid theory is one of the best models for the study of the motion of large charged molecules and low temperatures because the probability of movement of ions is smaller than in molten salts and also, an ionic association for charge transfer can be disregarded [23]. It is found that the simple lattice-HT theory can be usefully explained conductivity maxima [24]. The hole theory of liquids provides a simple and intuitive model which assumes that a liquid contains empty spaces or holes. In this model, space is considered to arise from thermally generated fluctuations in local density. The holes are randomly distributed and the radius of the average-sized hole ( $r_H$ ) is related to the surface tension ( $\gamma$ ). Once ( $r_H$ ) is known, the mobility of the hole can be obtained by the SE equation [25]. Therefore, the dire demand for thermophysical properties of ILs encouraged people to work out on these materials. Among the ILs, imidazolium-based ILs have received conspicuous attention. The selection of the imidazolium ring as a cation was due to its stability within oxidative and reductive conditions, the low viscosity of imidazolium ILs, and their ease of synthesis [26].

The surface tension of ILs is related to their pair potential function, radial distribution function, and liquid densities. We aim to evaluate a thermodynamic model for the prediction of the surface properties of imidazolium-based ILs by statistical mechanics. In this respect, contributions to surface tension from Lennard–Jones dispersion force were considered. Therefore, in this research, we evaluated the SE equation in combination with the hole theory for predicting the transport properties in particular surface tension of [amim]Br (ILs) (a= ethyl, butyl, pentyl, hexyl).

## 2. Theory

In this section, we have presented an argumentation about the main equation and model, which are used in this research. Previous research has shown that the SE equation is in good agreement with the diffusion behavior of ILs [5, 27]. It is becoming common practice to interpret the transport properties of a solute species using the SE equation and apply it to the investigation of the hole formalism in these materials [28-29]. The holes can be regarded in finite dilution and are independent of one another [25,30-33]. The SE equation is [31]:

$$D = \frac{k_B T}{6\pi r \eta} \quad (1)$$

Where  $D$  is the diffusion coefficient of the species,  $\eta$  is the viscosity coefficient,  $k_B$  is the Boltzmann constant,  $T$  is temperature, and  $r$  is the effective hydrodynamic radius (EHR) of the species molecule [32]. According to Eq. 1, one can estimate the viscosity coefficient by knowing the diameter of the molecule. We postulated this diameter is given by the HT through EHR.

It should also be mentioned that the primitive model was introduced [32] as an alternate view of the liquid phase and later extended by Bockris et al. [33], for use with molten salts. In this model, cavities occur at random positions and with random sizes because of thermal fluctuations, where the extent of cavity formation depends on the surface tension of the liquid [5]. In this theory, ions are assumed to migrate through empty spaces (holes) formed and destroyed by statistical fluctuations [5]. The HT is only suitable for ions movement that is smaller than the hole formed in its vicinity of it. The average size of holes in a liquid is calculated by the following equation [30]:

$$\langle r \rangle = 0.51 \left( \frac{k_B T}{\gamma} \right)^{\frac{1}{2}} \quad (2)$$

Where  $k_B$  and  $T$  have their usual meaning and  $\gamma$  is the surface tension of the liquid.

The values of Lennard-Jones's (LJ) contribution to surface tensions of ILs are calculated through Fowler, Kirkwood & Buff (FKB) [12] via;

$$\gamma^{LJ} = 3\pi\rho^2\varepsilon\sigma^4 \left[ \left( \frac{\sigma^2}{2r^{**2}} - \frac{\sigma^8}{4r^{**8}} \right) + \frac{r^{**3} - d^3}{3r^{**2}} \left( \frac{\sigma^2}{r^{*3}} - \frac{\sigma^8}{r^{*9}} \right) \right] \quad (3)$$

The reduced form of Eq.3 is as follows:

$$\gamma^* = 3\pi\rho^{*2} \left[ \left( \frac{\sigma^2}{2r^{**2}} - \frac{\sigma^8}{4r^{**8}} \right) + \frac{r^{**3} - d^3}{3r^{**2}} \left( \frac{\sigma^2}{r^{*3}} - \frac{2\sigma^8}{2r^{*9}} \right) \right] \quad (4)$$

Values of surface tension via the FKB equation are utilized for estimating the mean radius of the hole according to the HT. Insertion of the mean radius of the hole to SE equation on the one hand, and the calculated values of diffusion coefficients (obtained from Mean Square Displacement (MSD)) on the other hand give the viscosity coefficients. All of the implemented quantities in Eq. 3, have been taken from Ref. [13]. Indeed, the dimensionless parameters and the LJ parameters used in this study can be defined as:

$$T^* = \frac{kT}{\varepsilon} \quad (5)$$

$$\eta^* = \frac{\eta\sigma^2}{(m\varepsilon)^{\frac{1}{2}}} \quad (6)$$

$$D^* = \frac{D m^{\frac{1}{2}}}{\sigma \varepsilon^{\frac{1}{2}}} \quad (7)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (8)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (9)$$

$$d_{ij} = \frac{d_i + d_j}{2} \quad (10)$$

The cross-interaction parameters between different ions were calculated using the Lorentz-Berthelot mixing rules. In Eq. 3,  $\varepsilon$  is the depth of the potential well,  $\sigma$  is the finite distance at which the inter-particle potential is zero,  $d$  is the diameter of the hard-sphere which relates to  $\sigma$  of LJ fluid by the following equation [33]:

$$\frac{d_i}{\sigma_i} = \frac{1 + c_1 \left( \frac{k_B T}{\varepsilon_i} \right)}{1 + c_2 \left( \frac{k_B T}{\varepsilon_i} \right) + 1 + c_3 \left( \frac{k_B T}{\varepsilon_i} \right)^2} \quad (11)$$

### 3. Results and discussions

The numerical values of coefficients of Eq.11 and  $c_1$ – $c_3$  are dependent on the type of RDF applied. In this study,  $c_1=0.2977$ ,  $c_2=0.3316$  and  $c_3=0.001047$  coefficients were considered. The LJ parameter of anion and cation of ILs were taken from Ref. [13]. The LJ's contribution to the surface tension of four imidazolium-based (ILs) [amim]Br (a= ethyl, butyl, pentyl, hexyl) and the dimensionless surface tension ( $\gamma^* = \frac{\sigma^2 \gamma}{\varepsilon}$ ) were calculated by the above-mentioned equations and parameters and are given in **Table 1**.

**Table 1.** The Lennard Jones's contribution to surface tension of  $C_n$ mim]Br (n=2,4,5,6) ionic liquids and their reduced surface tension at 400 K.

Ionic Liquids	[C <sub>2</sub> mim] Br	[C <sub>4</sub> mim] Br	[C <sub>5</sub> mim] Br	[C <sub>6</sub> mim] Br
$\gamma^{LJ}$ (mN/m)	6.953	3.642	4.840	2.341
$\gamma^*$ ( $\gamma^* = \frac{\sigma^2 \gamma}{\varepsilon}$ )	0.206	0.203	0.396	0.173

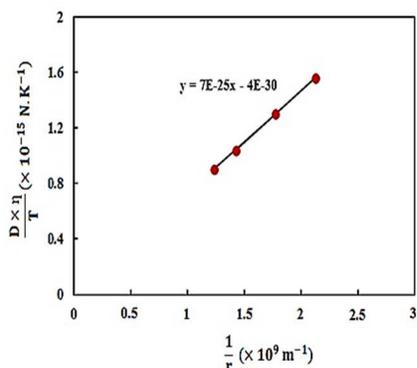
As can be seen from **Table 1**, [C<sub>2</sub>mim]Br IL has the highest surface tension. The surface tension exhibits a decrease as the alkyl group is lengthened. In the case of reduced surface tension, the same trend is observed, except for [C<sub>5</sub>mim]Br. The larger the alkyl chain on the cation, the smaller the surface tension for the ILs as a result of the increased Coulombic forces between the cation and the anion. The other parameters such as temperature, type of anions, etc., also affect surface tension values. Also, It should be noted that to calculate the exact value of surface tension, one has to consider the other contributions from hard-sphere repulsion, and the electrostatic interactions to surface tension. The obtained values of  $\langle r \rangle$  through Eq. 2, for ILs, are given in **Table 2**.

**Table 2.** The obtained average hole radius of C<sub>n</sub>mim]Br (n=2,4,5,6) ionic liquids.

Ionic Liquid	$\frac{1}{r}$ nm <sup>-1</sup>
[C <sub>2</sub> mim] Br	2.13
[C <sub>4</sub> mim] Br	1.43
[C <sub>5</sub> mim] Br	1.77
[C <sub>6</sub> mim] Br	1.23

As can be seen from **Table 2**, [C<sub>2</sub>mim]Br IL has the highest radius (the lowest value of  $\langle \frac{1}{r} \rangle$ ). According to equation 2, hole radius and surface tension have an opposite relationship with each other. Therefore, as the chain length increases, the radius of the hole increases and the surface tension decreases.

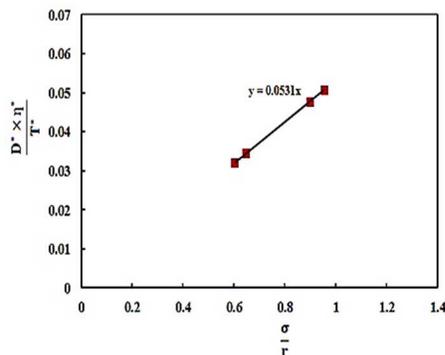
According to the best of our knowledge, there is no experimental data for the viscosity of ionic liquids of this series. However, to evaluate the viscosity values, the plot of  $\frac{D \times \eta}{T}$  versus  $\frac{1}{r}$  is depicted in **Figure 1**.



**Figure 1.** The plot of  $(D \times \eta)/T$  vs  $1/r$  for C<sub>n</sub>mim]Br (n=2,4,5,6) ionic liquids.

As shown in **Figure 1**, the slope of  $(D \times \eta)/T$  vs  $1/r$  for C<sub>n</sub>mim]Br (n=2,4,5,6) ionic liquids is  $7 \times 10^{-25}$ . According to the SE equation, if the slope of  $(D \times \eta)/T$  vs  $1/r$  is equal to  $k_B/6\pi$ , the validity of the used values is confirmed.

The plot of  $\frac{D^* \times \eta^*}{T^*}$  versus  $\frac{\sigma}{r}$  is depicted in **Figure 2**.



**Figure 2.** The plot of  $(D^* \times \eta^*)/(T^*)$  vs  $1/r^*$  for C<sub>n</sub>mim]Br (n=2,4,5,6) ionic liquids.

Moreover, based on dimensionless equations, the slope of  $\frac{D^* \times \eta^*}{T^*}$  versus  $\frac{\sigma}{r}$  is  $1/6\pi$  and the slope of the reduced plot is 0.0531. The aforesaid results of the slope are adequate.

#### 4. Conclusion

The tension at the surface of a liquid is one of the most notable intermolecular forces. Statistical thermodynamics provides a good opportunity to evaluate the thermodynamic model for representing the surface tension of ionic liquids. Tersely speaking, assessment of the SE equation is simply depicted by drawing of  $\frac{D \times \eta}{T}$  versus  $\frac{1}{r}$  and  $\frac{D^* \times \eta^*}{T^*}$  versus  $\frac{\sigma}{r}$ , simultaneously. Our test confirms the linearity of the diagram. Henceforth, the aforesaid approach for implementing the HT alongside the SE equation for ILs is fairly elaborate. Also, it is possible to calculate the viscosity of ILs using the Stokes–Einstein equation. The results indicated that the cation alkyl side chain length affects the surface tension of imidazolium-based ILs. In general, this work showed that knowing only the molecular parameters ( $\varepsilon$ ,  $\sigma$ ), the surface properties of ILs can be evaluated.

#### Appendix

##### Expressions for surface tension

Kirkwood and Buff's theory has explained the relationship between surface tension and intermolecular forces acting at an interface between two fluid phases based on statistical mechanics analysis. According to Fowler's approximation of KB theory, the surface tension of polyatomic fluids regardless of the contribution of the vapor density is given [12]:

$$\gamma = \pi \frac{\rho^2}{8} \int_0^\infty \left( \frac{\partial u(r)}{\partial r} \right) g(r) r^4 dr \quad (\text{A.1})$$

In this Equation,  $r$  is the intermolecular distance,  $\rho$  is the density of liquids,  $u(r)$  is the intermolecular pair potential, and  $g(r)$  is the radial distribution function (RDF). The common LJ pair interaction potential is:

$$u(r)_{ij} = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (\text{A.2})$$

Where  $r_{ij}$  is the distance between particles  $i$  and  $j$  and both  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are determined by using the Lorentz-Berthelot rules. The LJ potential parameters are used from Ref. [13] and the selected densities and diffusion of  $[\text{C}_n\text{mim}]\text{Br}$  ( $n=2,4,5,6$ ) are taken from Ref. [34].

#### Authors' contributions

All authors contributed to data analysis, drafting and revising of the paper and agreed to be responsible for all the aspects of this work.

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#### Declaration of competing interest

The authors declare no competing interest.

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#### Data availability

Data will be made available on request.

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