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The effect of various quantum mechanically derived partial atomic charges on the bulk properties of chloride-based ionic liquids

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ABSTRACT

Partial atomic charges using various quantum mechanical calculations for $[C_n mim]Cl$ ($n = 1, 4$) ionic liquids (ILs) are obtained and used for development of molecular dynamics simulation (MD) force fields. The isolated ion pairs are optimized using HF, B3LYP, and MP2 methods for electronic structure with 6-311+ +G(d,p) basis set. Partial atomic charges are assigned to the atomic center with CHELPG and NBO methods. The effect of these sets of partial charges on the static and dynamic properties of ILs is evaluated by performing a series of MD simulations and comparing the essential thermodynamic properties with the available experimental data and available molecular dynamics simulation results. In contrast to the general trends reported for ionic liquids with BF_4, PF_6, and iodide anions (in which restrained electrostatic potential (RESP) charges are preferred), partial charges derived by B3LYP-NBO method are relatively good in prediction of the structural, dynamical, and thermodynamic energetic properties of the chloride based ILs.

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1. Introduction

Room-temperature ionic liquids (ILs) define a new class of condensed matters because of their unique physicochemical properties. A molecular-based understanding of ILs poses a great challenge because the partial charge, the geometrical structure, and the electronic structure of the ions give rise to a complex interplay of molecular interactions [1].

Partial atomic charges, unlike the electron density, are not quantum mechanically observable, that is, they cannot be calculated from first principles. Hence, all methods for derivation of charge are ultimately arbitrary. They are, however, comparable based on the electrostatic performance of partial atomic charges produced for a given molecular system. Nevertheless, there is no universally accepted procedure, as the concept of partial atomic charge remains still arbitrary [2].

However, partial atomic charges are fundamental parameters for developing force fields in simulations and their accuracies play a substantial role in simulations of condensed phase properties. Under such circumstances, there is a significant debate about the best deal to determine effective atomic charges to simulate physical properties [3].

The most widely used methods for estimating atomic charges are derived from a least-square fit to the electrostatic potential (ESP) [4]. One of these methods, CHELP (CHarges from ELectrostatic Potentials), was initially developed by Chirlian and Francl, and then modified by Breneman and Wiberg as the grid-oriented CHELPG method which is less dependent upon molecular orientation than the original CHELP method in which partial atomic charges are fitted to reproduce the molecular ESP at a number of points around the molecule [5,6]. ESP is obviously one of the most useful properties in order to acquire proper partial atomic charges to model short-range as well as long-range molecule–molecule interactions [7]. On the other hand, natural bond orbital (NBO) analysis provides an accurate Lewis structure picture and charge density of a molecule using the highest percentage of orbital electron density representation [8].

Generating the charges using *ab initio* methods may give the most accurate representation of the charge distribution, provided that a suitable atomic basis set is used. The values of the atomic charges obtained by this method can be successively improved as the representation of the basis set improves. The reason is that the total molecular charge distribution depends on the nuclear positions and the agreement of the optimized geometries with the experimental ones will vary with the basis set applied. Although the *ab initio* derived charges fluctuate significantly with small basis sets, after one reaches a basis set of 6-3lG* quality,

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the electrostatic potential is close to convergent with respect to improvements in the basis set [3].

Development of force fields that provide satisfying description of both static and dynamic properties of the system is up to now a major open problem. Some molecular dynamics simulations have used force fields with reduced ionic charges to achieve this aim [9]. Morrow and Maginn, in their study on 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim]PF_6) were used a total charge of ±0.904 e on the basis of the quantum calculation of an ion pair in a vacuum [10]. Bhargava and Balasubramanian have explained that charge reduction leads to a faster dynamics for ionic liquids [11]. Holm and co-workers have presented detailed study of force field parameterization for 1,3-dimethylimidazolium chloride ionic liquid [12,13]. They performed MP2 electronic structure and DFT calculations on isolated ion pairs as well as Car–Parrinello MD simulation of 30 ion pairs. Their results indicated that absolute value of total ionic charge on cation and the anion are considerably less than unity [14].

Very recently, Mondal and Balasubramanian were carried out classical MD simulations of various ionic liquids with refined site charges obtained from condensed phase DFT calculations [15,16]. They indicated that calculated density, heat of vaporization, surface tension, diffusion coefficient and collective transport properties are in nearly quantitative agreement with experimental data [17]. Furthermore, we have carried out MD simulations with different atomic charges from various models in order to clarify the structure and dynamics of the pure ILs, mixtures of ILs with water, and alkane/ILs/water interfaces [18–20].

The CHELPG and NBO methods represent reasonable atom-centered charges for use in molecular simulations. However, there are still some issues that remain to be explored in choosing most appropriate partial atomic charges for simulation of periodic systems. A major aim of this work is to propose the most efficient method that gives rise to the most reliable charge values for the simulation of bulk properties of [C_1mim]Cl and [C_4mim]Cl ionic liquids. The paper is organized as follows: this introduction is followed by details of the methodology employed to calculate partial atomic charges, force field parameters and details of simulations. The third section is devoted to the description of results obtained and comparison with literature, and followed by conclusions section.

2. Computational methods

2.1. Ab initio calculations

The structure of each IL was optimized at different levels of theory: Hartree–Fock (HF) [21], hybrid density functional method (B3LYP) [22], and Möller–Plesset perturbation theory to the second-order (MP2) [23] using Gaussian 03 program [24], with 6-311++G(d,p) basis set. The basis set is selected large enough for the results to be independent of basis set. The computed structures of neutral ILs were checked for vibrational frequencies to assure the state of minimum energies is attained on the potential energy surface [25]. The structures of [C_1mim]Cl and [C_4mim]Cl ILs optimized with HF, B3LYP, and MP2 approaches are depicted in Figs. S1 and S2 (see Fig. 1 for atomic labels). Then, new sets of partial charges are assigned (to each IL) by two different procedures: (i) fitting to the electrostatic potential surface with the CHELPG procedure and (ii) carrying out population analysis using the NBO method, implemented in Gaussian 03.

2.2. Force field parameters

For the cationic part of ILs, the force field is in the form of explicit fully flexible all-atom force field developed by Canongia Lopes

et al. (CLaP) [26,27]. The electrostatic charges for dialkylimidazolium salts have been taken from our *ab initio* calculations (see Tables 1 and 2).

The slow dynamics of ILs and lack of attaining true equilibrium essentially lead to a large deviation on liquid state properties especially on simulated viscosity and surface tension. Polarizable force field increases the diffusion constant by a factor of three compared to the non-polarizable one [28]. On the other hand, due to high computational demands for the simulation of such complex liquids with ionic nature that dispersion interactions and hydrogen bonding play important roles, non-polarizable force fields are preferred [29].

The total interaction potential has the form

$$V^{tot} = \sum_{bonds} \frac{k_b}{2}(r - r_{eq})^2 + \sum_{angle} \frac{k_\theta}{2}(\theta - \theta_{eq})^2$$
$$+ \sum_{dihedrals} \sum_{i=1}^{3} \frac{V_i}{2}[1 + (-1)^{i-1}cos(i\Phi)]$$
$$+ \sum_{i=1}^{N-1} \sum_{j\rangle 1}^{N} \left\{ 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}} \right\} \quad (1)$$

where all terms have their usual meaning. The values of the parameters of Eq. (1) were taken from Refs. [27,30]. The cross term parameters ε_{ij} and σ_{ij} are given by combining and mixing rules, $\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}$ and $\sigma_{ij} = 1/2(\sigma_{ii} + \sigma_{jj})$, respectively.

2.3. Simulation details

For each liquid system, [C_1mim]Cl and [C_4mim]Cl, we performed simulation studies at ambient pressure (1.01325×10^5 Pa) using the DL_POLY program version 2.17 [31]. The equations of motion were solved using Verlet-Leapfrog integration algorithm, under the periodic boundary conditions. The Columbic long-range interactions were calculated using Ewald's method with a precision of 1×10^{-5}. The potential cut-off distance value of 16 Å was used for each simulation. For bulk simulations, a single ion pair with a geometrical structure optimized via *ab initio* calculation was replicated to obtain an ensemble containing 512 ion pairs of each liquid system under study. The simulation had to begin with short time step between 1×10^{-4} and 5×10^{-4} ps for 500 ps, and then followed by time step of 1×10^{-3} ps. After the initial equilibration with short time step, the temperature of the system was increased at intervals of 100 K up to 800 K. At each temperature, the simulation was performed for 2 ns under constant *NPT* conditions using the Nosé–Hoover thermostat/barostat algorithm [32,33] and the modification of Melchionna et al. [34], as implemented in the DL_POLY program. Then, the temperature of the system was decreased to 450 K at steps of 50 K. The relaxation times for the thermostat and barostat are 0.1 and 2.0 ps, respectively. After all these preliminary adjustments, the simulations were continued at this temperature for 8 ns in the canonical (*NVT*) ensemble, where the total energy of system indicates the state of equilibrium is reached satisfactorily. The obtained trajectory was considered equilibration and discarded. The *NVT* simulation was followed by 8 more ns collecting statistical data. The same simulation procedure is applied for each IL system while the quantum mechanically derived atomic charges were adopted in the force field.

3. Results and discussion

3.1. Atomic charges

The six sets of atomic charges derived in the current work are shown in Tables 1 and 2 for [C_1mim]Cl and [C_4mim]Cl, respectively. Atomic labels follow those in Fig. 1. The sum of partial