

Solvent structure of ionic liquid with carbon dioxide



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ABSTRACT

Structure of room temperature ionic liquid is studied based on a statistical mechanics, reference interaction site model. A flexibility in alkyl-chain of the imidazole cation is considered using a recently developed statistical mechanics theory, which is capable to treat conformational fluctuation of molecule. In addition, a simple procedure is presented to convert distribution as a function of distance between two sites into the distribution function represented in the corresponding dihedral angle.

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1. Introduction

Room temperature ionic liquid (RTIL) is a molten salt composed of bulky organic cation and anion with a melting point lower than room temperature [1,2]. In the decade, a wide range of applications have been studied because of its unique nature such as significantly low vapor pressure, thermal stability and a potential to provide distinctive environment different from common solvents.

Among them, dissolution of carbon dioxide (CO₂) into RTIL has been drawn much attention in recent years. By applying pressure, CO₂ is dissolved into RTIL with high concentration as contrasted to other non-polar molecules such as oxygen, nitrogen and so forth. Several studies including experiments [3–7] and computations have been performed so far. In particular, many computational studies on 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) are carried out using molecular dynamics and Monte Carlo simulation [8–10]. The details of the liquid structure is however, still veiled because of a difficulty in properly computing statistical ensemble caused by the strong Coulombic interaction between ions.

An integral equation theory for molecular liquid, reference interaction site model (RISM) [11,12], is a statistical mechanics to describe

liquid structure in terms of site–site pair correlation function. Thanks to its so-called analytical nature, RISM allows us to compute distribution function and thermodynamic quantities under a certain approximation. Moreover, it is computationally efficient compared to molecular simulation techniques. Chiappe et al. applied the RISM theory to study solvation process of gases into 1,3-dimethylimidazolium ([mmim][X]) [13,14]. In the theory, the shape of a molecule is represented with intramolecular correlation function ω . The function defines intramolecular distances (L) between atoms using delta function in real space, $\delta(r - L)$. This means that the molecular structure is fixed at a specific conformation and geometrical flexibility cannot be taken into account in the original RISM theory.

Among several efforts to improve this drawback, Yokogawa et al. recently extended the theory to enable to treat conformational fluctuation (flexible RISM), and applied it to chain molecular systems [15]. In the present study, this method is utilized to describe RTIL, especially flexibility in the alkyl-chain unit. Another important part of the present study is as follows: when considering four adjacent atoms labeled 1 through 4 (with fixed bond lengths and angles), the conformation is usually described as the dihedral angle around bond axis between the second and third atoms. In this theory, however, all the functions are described in terms of distance between consisting atoms (sites); An intramolecular correlation function representing the conformational distribution is a function of atom–atom distance. This situation often makes it difficult to understand the fluctuation of molecular structure. Here we present a procedure to convert a distribution function with respect to the distance between non-bonding two sites (corresponding to the atoms labeled 1 and 4) into the distribution as a function of the corresponding dihedral angle.

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2. Method

2.1. RISM theory

The equation of RISM is given by,

$$\rho h \rho = \omega * c * \omega + \omega * c * \rho h \rho, \quad (1)$$

where ρ , ω , h , c are number of density, intramolecular correlation function, total correlation function and direct correlation function, respectively. * is convolution integrals. ω describes molecular geometry, and its matrix element, $\omega_{\alpha\alpha'}(r)$, is related to two sites (atom or chemical group) α and α' .

$$\delta_{\alpha\alpha'} \delta(r) + (1 - \delta_{\alpha\alpha'}) \frac{1}{4\pi l_{\alpha\alpha'}^2} \delta(r - l_{\alpha\alpha'}), \quad (2)$$

where $\delta(r)$ is Dirac delta function, and $l_{\alpha\alpha'}$ is a constant to define the bond length (or distance) between sites α and α' . By definition, $\omega_{\alpha\alpha'}(r)$ is non-zero only when r equals to the constant value, $l_{\alpha\alpha'}$.

Because there are two unknown quantities in Eq. (1), h and c , one other equation is necessary to solve RISM equation. In the present study, Kovalenko–Hirata closure was adopted.

$$h_{\alpha\gamma}(r) = \begin{cases} e^{[-\beta u_{\alpha\gamma}^{(LJ)}(r) + \phi_{\alpha\gamma}(r) + h_{\alpha\gamma}(r) - c_{\alpha\gamma}(r)]} - 1, & \text{for } h_{\alpha\gamma} \leq 0, \\ \beta u_{\alpha\gamma}^{(LJ)}(r) + \phi_{\alpha\gamma}(r) + h_{\alpha\gamma}(r) - c_{\alpha\gamma}(r), & \text{for } h_{\alpha\gamma} > 0, \end{cases} \quad (3)$$

$u_{\alpha\gamma}^{(LJ)}(r)$ and $\phi_{\alpha\gamma}(r)$ are respectively short-range (Lennard-Jones) and Coulombic interactions between sites α and γ . The radial distribution function, $g_{\alpha\gamma}(r)$ is given by,

$$g_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) + 1 \quad (4)$$

In the present study, the liquid consisting of a variety of components, namely, cation, anion and CO₂. The extension of RISM theory to multi-component system is straightforward; The matrices are extended as follows.

$$\omega_{multi} = \begin{pmatrix} \omega_1 & 0 & \dots \\ 0 & \omega_2 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}, \quad \rho_{multi} = \begin{pmatrix} \rho_1 & 0 & \dots \\ 0 & \rho_2 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}, \quad (5)$$

Subscripts 1, 2, ... respectively correspond to molecular species in the system. $\rho_i (i = 1, 2, \dots)$ is a diagonal matrix whose element is the number density of molecular species.

2.2. Structural fluctuation in RISM

Yokogawa et al. generalized intramolecular correlation function ω to deal with conformational flexibility of molecule in liquid phase. In this treatment, deviation ($\Delta\omega$) from the function in an isolated molecule ($\omega^{(i)}$) is considered.

$$\omega \equiv \omega^{(i)} + \Delta\omega, \quad (6)$$

$$c^{(0)} \equiv c^{(i,0)} + \rho^{-1} \Delta c^{(0)}, \quad (7)$$

The direct correlation function $c^{(0)}$ is similarly given in the second equation. Using these quantities, the following equation is derived.

$$\Delta\omega_{\alpha\beta} = \sum_{\gamma\delta} \omega_{\alpha\gamma}^{(i)} * \Delta c_{\gamma\delta} * \omega_{\delta\beta}^{(i)} + \sum_{\gamma\delta} \omega_{\alpha\gamma}^{(i)} * \Delta c_{\gamma\delta} * \Delta\omega_{\delta\beta}. \quad (8)$$

Here, the subscripts α, β, \dots are sites in the same molecule. Eq. (8) is combined with a closure equation,

$$\omega_{\alpha\beta}(r) = \frac{1}{2} [\bar{\omega}_{\alpha\beta}(r) + \bar{\omega}_{\beta\alpha}(r)], \quad (9)$$

Table 1
Lennard-Jones parameters.

| Species | Site | Charge | $\epsilon/\text{kcal mol}^{-1}$ | $\sigma/\text{\AA}$ |
|---|------|--------|---------------------------------|---------------------|
| [bmim] ⁺ ^a | N1 | 0.071 | 0.170 | 3.250 |
| | C2 | 0.229 | 0.106 | 3.880 |
| | N3 | 0.133 | 0.170 | 3.250 |
| | C4 | 0.041 | 0.106 | 3.880 |
| | C5 | 0.096 | 0.106 | 3.880 |
| | C6 | 0.217 | 0.207 | 3.775 |
| | C7 | 0.024 | 0.118 | 3.905 |
| | C8 | 0.118 | 0.118 | 3.905 |
| | C9 | 0.118 | 0.118 | 3.905 |
| | C10 | -0.047 | 0.175 | 3.905 |
| [PF ₆] ⁻ (U.A.) ^b | | -1.000 | 0.399 | 5.600 |
| CO ₂ | C | 0.700 | 0.058 | 2.785 |
| | O | -0.350 | 0.165 | 3.064 |

^a Reference [9].

^b Reference [13].

$$\bar{\omega}_{\alpha\beta}(r) = \omega_{\alpha\beta}^{(i)}(r) \exp \left[\sum_{\gamma} \Delta c_{\beta,\gamma}^{(0)} * \Delta\omega_{\gamma\alpha}(r) + \sum_{\gamma} \rho_{\gamma} c_{\beta,\gamma} * h_{\gamma\alpha}(r) + C \right]. \quad (10)$$

By solving these equations, h , c and extended ω are obtained. The conformational distribution of the molecule is represented in ω as a function of site-site distance r .

2.3. Computational details

RISM theory was applied to ionic liquid, [bmim][PF₆] with and without CO₂. The number densities of [bmim]⁺, [PF₆]⁻ and CO₂ were taken from literature [16], corresponding to an experimental condition of CO₂-solved [bmim][PF₆] (the mole fraction was 0.47) under 5.0 MPa. Specifically, the densities of [bmim]⁺, [PF₆]⁻, CO₂ were 0.002552642 molecule \AA^{-3} , 0.002552642 molecule \AA^{-3} and 0.002263664 molecule \AA^{-3} , respectively (Table 3). For the pure [bmim][PF₆] system, the density was set to 0.002733676 molecule \AA^{-3} for each ion. The temperature was set to 313.15 K in the both systems.

All the force field parameters were listed in Table 1. United atom model, where all the hydrogen atoms were fused to carbon atom, was employed (Fig. 1) with the optimized geometry using MP2/6-311++G(d,p). [PF₆]⁻ was modeled as a single site. All the atoms were explicitly treated in CO₂, where the C–O bond length was 1.161 \AA .

A structural flexibility was treated in the butyl group of [bmim]⁺. Three dihedral angles, namely rotations around N1–C7, C7–C8 and C8–C9 bond axes were considered. The potential energy functions for them were given by,

$$V(\phi) = V_0 + \sum_{n=1}^3 V_n [1 - (-1)^n \cos(n\phi)]. \quad (11)$$

The parameters taken from the literature were listed in Table 2. All other bond lengths and angles were fixed. $\omega^{(i)}$ for an isolated molecule is computed using Monte Carlo simulation.

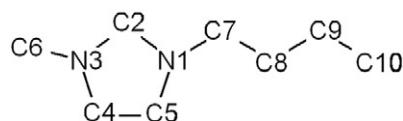


Fig. 1. United atom model of [bmim]⁺.

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