

Fast solute diffusivity in ionic liquids with silyl or siloxane groups studied by the transient grating method



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ABSTRACT

To achieve ionic liquids (ILs) that show fast solute diffusivity independent of viscosity domination, sixteen ILs containing Si or Si–O–Si groups (SiILs) were synthesized. Diffusion coefficients of three solute molecules with different molecular sizes, i.e., CO, diphenylacetylene, and diphenylcyclopropanone, were determined in SiILs using the transient grating method and the results were compared to other solvent system. SiILs showed distinguishably faster diffusivity for the smallest solute, CO, than conventional ILs at the same viscosity, particularly in the high viscosity region. Based on previous results and our estimation, three plausible factors exist that contribute to the faster solute diffusivity in SiILs, i.e., the flexibility of the Si or Si–O–Si group, decreased interaction between the cation and the solute, and increased free volume because of the bulky structure.

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1. Introduction

Ionic liquids (ILs) are salts that are liquid at ambient temperature. Since they are composed solely of ions and have several outstanding characteristics as solvents, such as negligible flammability and vapor pressure, high thermal/chemical/electrochemical stabilities, and unique solubility, ILs are potentially useful as new types of chemical reaction media and electrolytes. Considering these applications, solute diffusivity in solvents is a very important factor, as exemplified by diffusion-controlled reactions. Classically, a solute diffusion is represented by the Stokes–Einstein (SE) equation.

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

where k_B is the Boltzmann constant, T is the temperature, C is a constant theoretically ranging from 4 (slip boundary condition) to 6 (stick boundary condition), η is the viscosity, and r is the hydrodynamic radius of the solute.

Since most ILs exhibit high viscosity (typically 10^1 – 10^3 mPa s) compared to conventional organic solvents (typically 10^{-1} – 10^1 mPa s), designing low-viscosity ILs that facilitate solute movement is a significant challenge that many studies have been devoted

[1–5]. Molecular designs that control ion size, flexibility, and asymmetry of both cations and anions strongly affect the viscosity of ILs. However, attempts to lower the viscosity are limited due to the intrinsically strong Coulombic interactions that make them viscous. Since the SE equation is known to break down particularly for small solute molecules, which display higher diffusivity, we propose another approach to achieve high solute diffusivity in ILs, which is to design ILs that enhance solute diffusivity that are less independent of viscosity than theoretically predicted.

In this sense, we focused on silyl or siloxane structures seen in silicone oil. It is widely known that solute molecules in silicone oil have higher translational and rotational diffusivity than those predicted by the SE equation [6–14]. For example, the diffusion coefficients of phthalic anhydride in polydimethylsiloxane were estimated from fluorescence quenching rates of the solute, and the values were up to 10^6 times higher than those calculated from the SE equation in the high viscosity region (10^6 mPa s) [7]. High flexibility and large free volume are considered to account for these features of silicone oil. In fact, the introduction of silyl or siloxane structures in ILs (SiILs) was first reported by Shirota et al. [15–16]. Since then, many groups have synthesized new types of SiILs and revealed their characteristics [17–28]. In the first paper [15], a novel imidazolium-based cation with a trimethylsilylmethyl group was synthesized and its physical properties were compared to an IL with a neopentyl group on the cation. The only difference in structure between these ILs is one atom on the side

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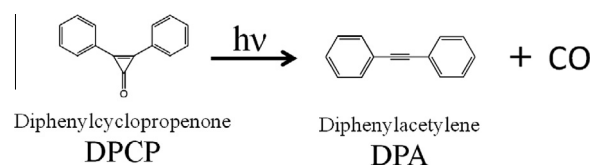
chain, with silane in the trimethylsilylmethyl group and carbon in the neopentyl group. A significant decrease in the viscosity was observed on the substitution of silane. Later, an IL with a siloxane group was synthesized by the same group that showed similar viscosity to the IL with a silyl group [16]. It was revealed by electron density calculations and Raman-induced Kerr effect spectroscopy that the viscosity decrease stemmed from the decrease in cation–anion interactions. Niedermeyer et al. investigated the flexibility of siloxane groups attached to imidazolium cations through density functional theory (DFT) calculations [29]. Their results showed that the rotational barriers of the side chain were lower for the siloxane group than that for the butyl group. These findings for both silicone oil and Si or Si–O–Si group containing ILs imply that SiILs are promising in terms of high solute diffusivity.

In this paper, we synthesized sixteen SiILs (Fig. 1) from four cations, 1-methyl-3-propyltrimethylsilylimidazolium (propylSiIm), 1-methyl-3-methylpentamethylidisiloxyimidazolium (SiOSiIm), N-methyl-N-propyltrimethylsilylpyrrolidinium (propyl-SiPyrr), and N-methyl-N-methylpentamethylidisiloxypyrrolidinium (SiOSiPyrr), paired with four anions, bis(fluorosulfonyl)imide (FSI), bis(trifluoromethanesulfonyl)imide (TFSI), bis(pentafluoroethanesulfonyl)imide (BETI), and hexafluorophosphate (PF₆). The solute diffusions of these SiILs were then compared with those of silicone oils as well as of IL and molecular solvent systems previously reported [30–31]. Solute diffusions were measured using the transient grating (TG) method. The TG method has been employed to determine the diffusion coefficients of photoreacted and photoproducted molecules in solutions and proven to be effective even in ILs as high-viscosity media [30–32]. We used diphenylcyclopropanone (DPCP), which produces diphenylacetylene (DPA) and CO by photoreaction (Scheme 1). This means that the diffusion coefficients of three solute molecules with different molecular sizes can be detected simultaneously. The solute diffusivity and factors that dominate the diffusivity in SiILs are discussed based on the (fractional) SE relationship.

2. Experimental section

2.1. Sample preparations

SiILs were synthesized according to a conventional procedure [15]. All starting materials, i.e., 1-methylimidazole (ACROS), N-methylpyrrolidine (ACROS), 3-chloropropyltrimethylsilane (Gelest), chloromethylpentamethylidisiloxane (Gelest), potassium bis(fluorosulfonyl)imide (Kanto Kagaku), lithium bis(trifluoromethanesulfonyl)amide (Kanto Kagaku), lithium bis(pentafluoroethanesulfonyl)imide (Kishida Kagaku), and potassium hexafluorophosphate (Kanto Kagaku) were used as received. First, chloride salts were obtained by the quaternization of amine derivatives with Si or Si–O–Si containing compounds terminated with a chlorine atom. The reactions were typically carried out in acetonitrile at 353 K for 48 h under an Ar atmosphere. Appropriate purifications were performed for the obtained chloride salts such as washing with ethyl acetate, recrystallization, and decolorizing



Scheme 1. Photodissociation reaction scheme of DPCP.

with activated charcoal. SiILs were prepared from the corresponding chloride salts by ion exchange with a lithium or potassium salt in an appropriate solvent. The obtained liquids were washed with distilled water several times until they passed the AgNO₃ test and decolorized with activated charcoal to minimize absorbance at 355 nm (typically less than 0.3 with a path length of 1 cm). A detailed procedure of the preparation of [propylSiIm][FSI] is described in Supporting Information as an example. All SiILs except [propylSiPyrr][FSI] (m.p. = 328–333 K), [propylSiPyrr][PF₆] (m.p. = 388–393 K), [SiOSiPyrr][BETI] (m.p. = 333–338 K), and [SiOSiPyrr][PF₆] (m.p. = 378–383 K) were liquid at room temperature. The final yields ranged from 22% to 72%. The SiILs were characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopies (JEOL JNM-ECS400 or JNM-ECA600, see Supporting Information for details). The cation and anion structures of the SiILs are shown in Fig. 1. Conventional ILs with alkyl groups (AILs), 1-allyl-3-ethylimidazolium (AElm), N-methyl-N-propylpyrrolidinium (P1,3), and N-methyl-N-butylpyrrolidinium (P1,4), paired with TFSI anions were purchased from Kanto Kagaku. Silicone oils as reference materials with various viscosities (i.e., KF-96-10CS, KF-96-50CS, KF-96-100CS, and KF-96-500CS, the numbers expressed as xxCS are kinematic viscosity at 298 K) were purchased from Shin-Etsu Silicone. The samples were dried under vacuum overnight before use.

2.2. Viscosity and density measurements

Viscosity of the ILs were measured with a cone/plate viscometer (Brookfield LVDV-II). For room temperature measurements, the temperature was stabilized at 296 ± 1 K. The temperature was controlled between 294.2 K and 333.2 K for variable temperature experiments with 0.1 K accuracy. Density measurements were conducted with Anton Paar, DMA 35 at 298.2 ± 0.1 K.

2.3. TG measurements

For the TG measurements, DPCP was dissolved in the ILs to achieve an absorbance of 1.5 with a 0.5 cm or 1 cm optical length cell at 355 nm, which roughly gives a concentration of 10⁻³ M. This concentration would be dilute enough to approximate mutual-diffusion coefficients obtained from TG experiments by self-diffusion coefficients of solute molecules. The sample solution was filtered to remove any undissolved solutes and dust before use.

The experimental setup for TG measurements was similar to those reported elsewhere [31]. Briefly, the third harmonic pulse (355 nm) of the neodymium-doped yttrium aluminum garnet

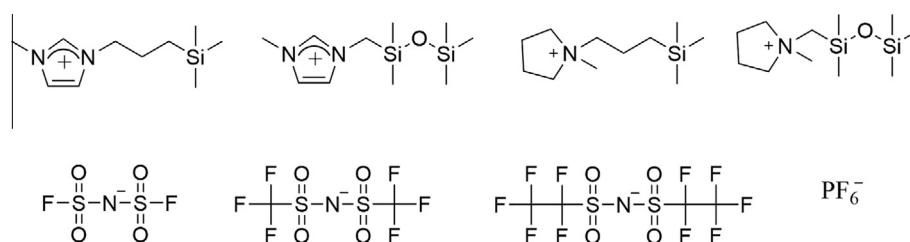


Fig. 1. Molecular structure of the cations and anions for SiILs.

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