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Slowdown of H/D Exchange Reaction Rate and Water Dynamics in Ionic Liquids: Deactivation of Solitary Water Solvated by Small Anions in 1-Butyl-3-Methyl-Imidazolium Chloride

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The H/D exchange reaction and the rotational dynamics of heavy water (D_2O) are studied at 50 °C in the ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), in the [D_2O] range of 3−55 M. The initial H/D exchange rates are observed as 1.0×10^{-7}, 4.5×10^{-6}, 1.0×10^{-5}, 4.1×10^{-5}, 1.1×10^{-4}, and 3.7×10^{-4} s^{-1}, respectively, at [D_2O] of 2.8, 7.1, 8.1, 11, 15, and 25 M. The rate is very slow and less than 10^{-5} s^{-1} at [D_2O] below ~7 M. It steeply increases to the order of 10^{-4} s^{-1} for 7 M < [D_2O] < 10 M, and linearly increases with [D_2O] in the more water-rich region. The intercept of the linear region at [D_2O] = ~9 M is interpreted by considering that each chloride anion deactivates 1.6 equiv water molecules due to the strong solvation. Correspondingly, the rotational correlation time of D_2O at [D_2O] < 7 M is 1 order of magnitude larger than that in water-rich conditions.

1. Introduction

Ionic liquids (ILs), which provide a strong local electric field, are attracting much interest as a new and unique reaction medium for its nonvolatility and phase separation behavior with organic solvents and/or water.[1−4] Although much efforts are being made for the optimization of reaction yields in ILs, so far there have been reported only a few kinetic studies.[5,6] Kinetic studies are essential for the reaction pathway control and the yield optimization. In this letter, we focus on the correlation between the kinetics of H/D exchange and the rotational dynamics of D_2O in hydrophilic 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and get insight into the solvation of water by the solvent ions. The H/D exchange reaction rate can reflect sensitively how strongly water is solvated by the small chloride anions via the hydrogen bonding. By covering a wide range of water concentrations (3−55 M), we have demonstrated here that solitary water is deactivated by orders of magnitude compared with water in water-rich conditions. At low concentration, water is solitary in the sense that water−water contact is negligible and is bound strongly by the solvent ions. It is shown that the reactivity of water in the IL can be tuned by the concentration (number density) of water in a way similar to supercritical water.[7−9]

The strength of water−anion interactions in ILs is to be reflected quantitatively by the dynamics of water. Therefore we expect that solitary and bound water is slowed down substantially in the rotational dynamics in a manner analogous to that in the H/D exchange reaction. The dynamics of larger fluorescence molecules has been investigated in ILs[10,11] in relation to the solvation dynamics while that of water has been studied only computationally by Hanke and Lynden-Bell.[12] They calculated the rotational correlation time at a rather high temperature of 127 °C and water concentrations of 25, 50, and 75 mol % by means of molecular dynamics simulation and reported that rotational dynamics slows down monotonously with decreasing water concentration. Here, we apply ^2H NMR spectroscopy to determine the rotational correlation time at 50 °C over a wide range of D_2O concentrations from 1 (solitary conditions, 50 mM) to 80 mol % (18 M). We have succeeded in demonstrating the excellent parallelism between the rotational dynamics slowdown and the H/D exchange deactivation.

ILs often are contaminated with a small amount of acids, metals, and/or absorbed water. Uncontrolled impurities can significantly influence the reaction rates and lower the reproducibility. To prevent acid or base impurities from influencing the H/D exchange reaction, we have introduced a neutralization titration method and have certified a high level of neutrality of the used IL.

2. Experimental

Ionic liquid [bmim][Cl] (99%) was obtained from Solvent Innovation and purified before use as described below. D_2O (99.9 atom%) was obtained from Nakalai and was used as received. Reaction solutions of D_2O in [bmim][Cl] were prepared in a dry box to avoid atmospheric H_2O and CO_2. A reactor made of quartz tube was 2.5 mm i.d., 4.0 mm o.d., and ~8 cm long. A sample was heated at 50 °C in an NMR spectrometer (JEOL ECA400, magnetic field strength of 9.4 T) and ^1H NMR spectra were observed in situ at time intervals of 1−100 min. The deuteration ratio of the imidazolium cation was determined by the ^1H peak intensity of the H/D exchangeable proton in the cation. The rotational correlation time of D_2O was determined by ^2H spin−lattice relaxation measurements between −40 and 50 °C using two NMR spectrometers (JEOL ECA 400W, 9.4 T and ECA 600, 14.1 T).[13] The diffusion

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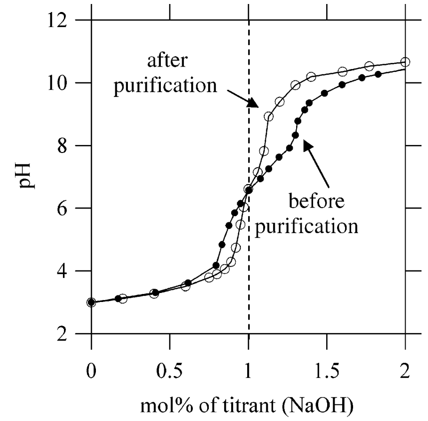


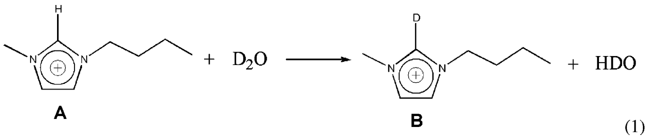
Figure 1. The neutralization titration curve for the [bmim][Cl], before purification (filled circles) and after recrystallization three times (open circles). Before the titration, 1.00 mmol of [bmim][Cl] was dissolved in 10 mL of H_2O and 0.0100 mmol of HCl was added. The buffering region around pH = ∼7 corresponds to the neutral imidazole.

coefficient of the 1-butyl-3-methylimidazolium cation was determined by pulsed field gradient spin−echo ^{1}H NMR at 400 MHz.[14]

The ionic liquid was purified by recrystallization three times in dry acetone−acetonitrile (10:1 by weight) mixture. The yield of purified crystal was ∼60% for each recrystallization process; the solution saturated at 40 °C was cooled down to 20 °C. The purity was assessed by the neutralization titration. The titration curves before and after the recrystallizations are shown in Figure 1. A buffering region around pH = ∼7 in the titration curve before the purification indicates the presence of ∼1 mol % neutral imidazole as an impurity (the acid dissociation constant $pK_a = 6.0$ for imidazole[15]). After the above-mentioned purification, the titration becomes sharper by a factor of 10. Thus, impurities are sufficiently removed and the neutrality has been highly attained.

3. Results and Discussion

3.1. Kinetics of H/D Exchange. The solute D_2O in [bmim]-[Cl] solvent undergoes the following H/D exchange reaction



(1)

It has been found that no protons other than the one attached to the 2 position of the imidazole ring participate in the H/D exchange under the reaction conditions studied here. We first try to analyze the reaction kinetics based on the second-order rate law:

$$\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k(2[D_2O] + [HDO])[A] \tag{2}$$

Here the brackets [ ] stand for the molar concentration, A and B are the undeuterated and deuterated cations (see eq 1), respectively, and k is the H/D exchange rate constant. There are two species of deuterated water, D_2O and HDO. Because they are in equilibrium, $2[D_2O] + [HDO]$ corresponds to the concentration of the deuteron. By denoting the deuteron concentration of water by $[D_{water}]$, eq 2 is rewritten as

$$\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k[D_{water}][A] \tag{3}$$

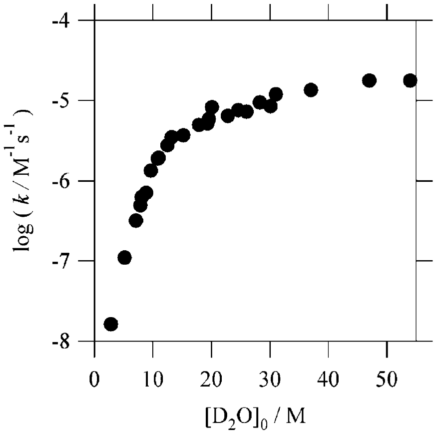


Figure 2. The plot of the apparent second-order rate constant k defined by eq 2 against water concentration. Note that the solution is dominated by the ionic liquid in terms of volume fraction when $[D_2O] < 30$ M; the molecular volume of water is much smaller than that of the ionic liquid. The apparent rate constant suddenly drops off at $[D_2O]$ ∼15 M.

The initial reaction rate v_0 of the H/D exchange is then given by

$$v_0 = \left.\frac{d([B]/[A]_0)}{dt}\right|_0 = \left.\frac{d\alpha}{dt}\right|_0 = k[D_{water}]_0 = 2k[D_2O]_0 \tag{4}$$

where the subscript 0 indicates the zero reaction time and α is the deuteration ratio of the cation. If the H/D exchange kinetics obeys the rate law given by eq 2, the value of k would not depend on the value of $[D_2O]_0$. We then determined the rate constant k on the basis of eq 4 by varying $[D_2O]_0$. The logarithm of k is plotted against $[D_2O]_0$ in Figure 2. Evidently, k is not constant against the $[D_2O]_0$ variation. The value of k changes by orders of magnitude depending on $[D_2O]_0$ in the range of 3−20 M, above which it is gradually saturated to the level of the dilute aqueous solution of [bmim][Cl]. Thus, eq 2 is not a valid equation. We need to establish a new rate law to explain the fact that the reactivity of water dramatically decreases as $[D_2O]_0$ decreases.

We can understand to what extent water is deactivated at the water-poor composition by considering the strong Coulombic solvation of water by the small chloride anion. The water molecules solvated by the anion (“bound” water molecules) are hydrogen bonded at the hydrogen sites, so they have little chance to exchange their deuteron atoms with the protons in the imidazolium cations. When the water concentration is low, almost all of the water molecules are solitary and bound, and the H/D exchange rate is very slow. As the water concentration $[D_2O]_0$ is high, on the other hand, the chloride anions are fully hydrated with water molecules, and the excess water molecules have a high activity for the H/D exchange.

On the basis of the above consideration, we propose a new rate equation. When we take x as the number of bound water molecules around a chloride anion (the coordination number), the initial rate v_0 of the H/D exchange is expressed as

$$v_0 = \left.\frac{d\alpha}{dt}\right|_0 = k^*[D^*_{water}]_0 \tag{5}$$

where the symbol D^*_{water} represents the deuteron atom of the active (unbound) water molecules and is given by

$$[D^*_{water}]_0 = 2[D_2O]_0 - 2x[Cl^-] \tag{6}$$

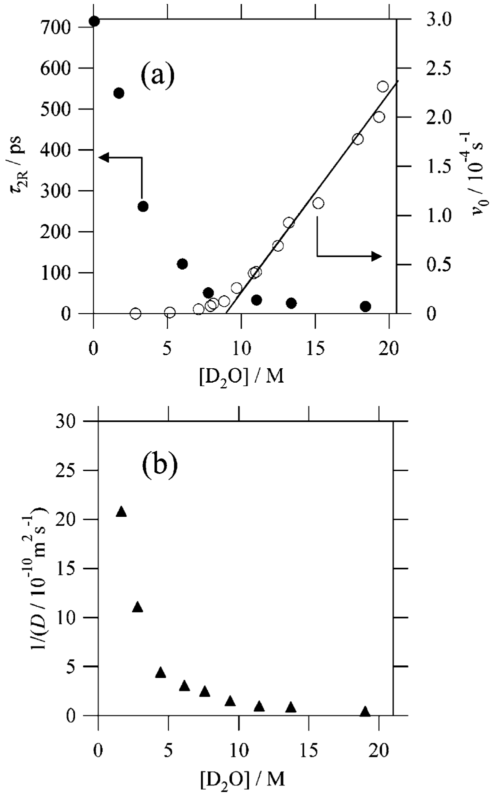


Figure 3. (a) The initial rate v_0 of the H/D exchange (open circles) and the rotational correlation time τ_{2R} (filled circles) as a function of water concentration. (b) The reciprocal of the diffusion coefficient D of the 1-butyl-3-methylimidazolium cation against water concentration.

k^* is the rate constant for the active water molecules. The value of x is regarded as constant as long as the water concentration is high enough to occupy all the bounding sites of the chloride anion. To determine the value of k^* and x, we plotted the initial H/D exchange rate v_0 at 50 °C against the initial water concentration $[D_2O]_0$ in Figure 3a. The exchange rate begins to linearly increase with a steep slope as $[D_2O]$ is increased above ~10 M. This indicates that the concentration of unbound water (free from the direct solvation by the anion) $[D^*_{\mathrm{water}}]$ linearly increases and contributes to the H/D exchange rate according to eq 5. We can determine the coordination number x as the mole ratio of D_2O to Cl^- when the reaction rate begins to rise. As is seen from Figure 3a, the intercept of the linear region of the plot to the horizontal axis gives the $[D_2O]$ value of 8.9 M. This molar concentration corresponds to the mole ratio ~1.6 of D_2O to the IL and thus we obtain $x = 1.6$. The rate constant k^* is represented by the slope of the line and is 1.0×10^{-5} M^{-1} s^{-1}.

3.2. Rotational Dynamics of D_2O. In this section, we investigate the relationship between the rotational dynamics and the H/D exchange kinetics of the solute water in IL covering a wide range of the water concentration. We determine the rotational correlation time τ_{2R} of D_2O in [bmim][Cl] by means of ^2H NMR relaxation measurements.[13] The value of τ_{2R} at 50 °C is plotted against $[D_2O]$ in Figure 3a. The rotational correlation time of water is by 2 or 3 orders of magnitude larger than that in neat conditions (1.34 ps).[16] As seen from Figure 3a, the concentration dependence of the water rotational dynamics corresponds well to that of the H/D exchange reactivity. The value of τ_{2R} changes rapidly by a factor of ~10 at the lower water concentrations ($[D_2O] <$ ~8 M), while it changes fairly slowly at the higher water concentrations. The crossover concentration (~8 M) of τ_{2R} is in agreement with the concentration at which the steep increase of the H/D exchange reactivity was observed. This good correspondence indicates that the rotational dynamics of water in the IL can be understood in terms of the solvation just as in the case of the H/D exchange reaction kinetics.

One may consider that the increase of τ_{2R} in water-poor conditions arises from the high viscosity of the IL. To scrutinize this point, we measured the diffusion coefficient D of the imidazolium cation instead of the viscosity at 50 °C by varying $[D_2O]$ up to 20 M.[17,18] $1/D$ is proportional to the viscosity according to the Einstein−Stokes equation. Thus, if the rotational dynamics is controlled by the viscosity of the system, τ_{2R} would be propotional to $1/D$. We plotted $1/D$ against $[D_2O]$ in Figure 3b. As can be seen, the water concentration dependence of τ_{2R} does not agree with that of $1/D$ at water-poor conditions. Thus, the rotational dynamics is dominated by the strong solvation of water by the anion rather than the viscosity. In the case of the H/D exchange reaction, the viscosity does not directly influence the kinetics, because the observed reaction rate in Figure 2 is ~10 orders of magnitude smaller than the diffusion controlled rates (10^7 M^{-1} s^{-1}).

The present study on the H/D exchange reaction kinetics and the rotational dynamics of water in the IL allows us to predict the following general features of water in chemical reactions in IL. (1) The reactivity of water is tunable over orders of magnitude by varying the water concentration. The water molecules participate in reactions as a reactant when the water content is increased above the value determined by the coordination number (1.6) of the chloride anion. (2) In a water-poor composition (the water concentration of lower than ~7 M), water molecules are deactivated and make no significant contributions to reactions in IL as a reactant.

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