Kinetic Salt Effects on an Ionic Reaction in Ionic Liquid/Methanol Mixtures —Viscosity and Coulombic Screening Effects—

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The kinetic salt effect on the disproportionation reaction between diiodide anions in methanol has been examined using two ionic liquids and one inorganic salt. The ionic reaction was accelerated significantly, depending on the cation of the salt, and the ionic liquids enhanced the reaction more effectively. At higher concentrations the reaction rates decrease owing to increasing viscosities.

Room-temperature ionic liquids have very unique properties, such as negligible vapor pressure, high thermal stability, and ionic conductivity. One application of ionic liquids is in electrochemical devices, such as electric double-layer capacitors,[1] lithium batteries,[2] fuel cells,[3] and dye-sensitized solar cells.[4] In these devices, ions and ionic reactions play important roles. It is well known that the addition of salt increases or decreases the rates of ionic reactions, depending on whether the reactant charges are like or unlike each other. These effects have been treated with Debye–Hückel theory, alhough the applicable ion concentration range is limited to about 0.01 mol/L. In contrast, the concentrations of ions in ionic liquids may be in the range of 2 to 5 mol/L. Therefore, ionic reactions under such high ionic strength conditions are of interest. In our previous study,[5] the rate constants for the disproportionation of diiodide anion radicals in ionic liquids were found to be close to the diffusion limit for *neutral* molecules. Consequently it was inferred that electrostatic repulsion between the diiodide anion radicals is weakened by the Coulombic screening in the ionic liquids.

In the present study, we examine the kinetic salt effect on the reaction between diiodide anion radicals in methanol using a wide concentration of ionic liquid salts. To extract the specific salt effect of ionic liquids in organic solvent, we also used the inorganic salt lithium bis(trifluoromethylsulfonyl)amide (LiTFSA) for comparison. Using the ionic liquids it is possible to examine the salt effect under very high mole fraction conditions.[6]

The experimental system is the same as previously described.[5] Nanosecond transient absorption kinetics measurements were performed with a 248 nm KrF excimer laser (Lambda Physik, Lextra 100, 15 ns pulse duration) for excitation.

N,*N*,*N*-Trimethyl-*N*-propylammonium bis(trifluoromethyl sulfonyl)amide (TMPA–TFSA) and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethylsulfonyl)amide (PP13–TFSA) were used as electrolytes, and these were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). For the kinetics measurements, aliquots of the KI-containing methanol solution were placed in screw-capped, 1-cm quartz cuvettes. The viscosity of the solution was measured with a viscometer (Brookfield, DV-II+Pro, CP-40).

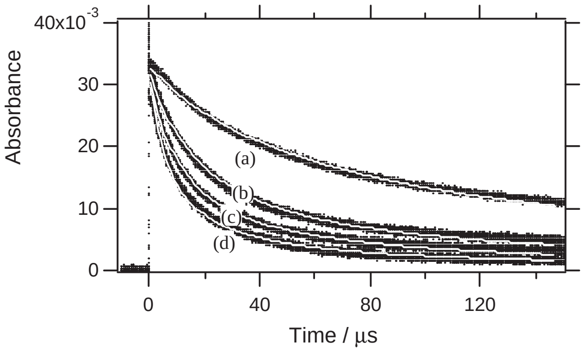

Figure 1. Decay traces of diiodide monitored at 700 nm: The concentrations of TMPA–TFSA are (a) 0, (b) 7.2, (c) 32, and (d) 74 mM. Solid lines are fitting results to the second-order decay.

As reported in the previous work,[5] the I_2^- species can be produced by the 248-nm laser excitation of the iodide CTTS absorption band. Figure 1 shows examples of transient absorption signals at 700 nm with different concentrations of TMPA–TFSA in methanol. These decay signals correspond to the following disproportion reaction:

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \qquad (1)$$

As the concentration of TMPA–TFSA increases, the decay rate becomes faster, indicating that the ionic liquid TMPA–TFSA accelerates the reaction rate between I_2^- anion radicals. Because the I_2^- anions are expected to be surrounded by TMPA cations, the Coulombic repulsion between the I_2^- anion radicals is screened. Therefore, the I_2^- anion radicals can easily approach each other to react. The rate constants for the reaction of I_2^- anion radicals were extracted by the fitting of the decay signals and using the extinction coefficient of I_2^- as reported in the previous work.[5] In Figure 2, $\log(k/k_0)$ was plotted against the square root of the ionic strength I for three different salts. Where, k and k_0 are rate constants with and without salt. At low ionic strength, the values of $\log(k/k_0)$ are proportional to $\sqrt{I}$, indicating that the Debye–Hückel limiting law could be applicable. However, as the ionic strength increases, the plots deviate from a straight line. As can be seen in Figure 2, the effect of ionic strength on the rate constants depends on the kind of salts used. Because these salts are composed of the common anion TFSA, the difference in the effect of ionic strength can

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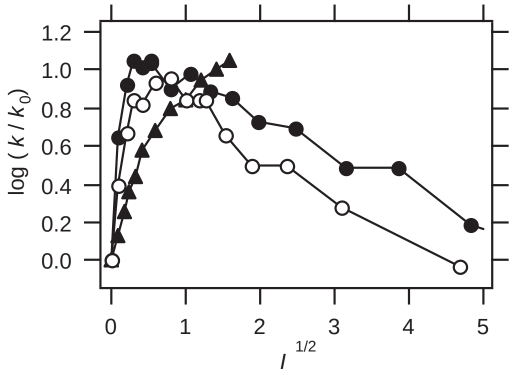

Figure 2. Relation between $\log(k/k_0)$ and square root of the ionic strength I: Filled circle, TMPA–TFSA; open-circle, PP13–TFSA; filled triangle, Li–TFSA.

be attributed to specific effects of the cations. At low ionic strength, TMPA cation increases the reaction rate most effectively, while Li cation is less effective. There are a few possibilities to explain this result, such as screening effects, reduction of I_2^- anion mobility, and electrolyte ion association. At high salt concentrations, it can be expected that the degree of dissociation of Li–TFSA is lower than for the ionic liquids; hence, the kinetic salt effect may be less effective in Li–TFSA than in the ionic liquids. The screening effect on the electrostatic repulsion between I_2^- anions may depend on the size of the cations. A larger cation could effectively screen the electrostatic repulsion between I_2^- anions. On the other hand, the mobility of I_2^- may be reduced by asymmetric effects of ion solvation around I_2^-. Because the smallest cation among the used salts is Li^+, the Li^+ cation may have strongest electrostatic interaction with I_2^- anion. This may lead to a decrease in the mobility of I_2^-. The effect of salt on the diffusion coefficient of hydrated electron has been studied previously, and the diffusion of hydrated electron decreased with the addition of salt.[7]

A notable contrast in the kinetic salt effects for TMPA–TFSA and PP13–TFSA at higher salt concentrations (0.5–1.5 M) is that the values of $\log(k/k_0)$ decrease with increasing salt concentration, whereas no such decrease was observed for Li–TFSA in the same concentration range. Since the ionic liquids are miscible with methanol, it is possible to explore the entire range of mole fraction. The solution viscosity rises significantly at higher proportions of ionic liquid. Accordingly, the viscosities were measured at each concentration used and the rate constants were plotted against the inverse of the viscosity η in Figure 3. The solid line in the figure is the expectation according to eq 2 for diffusion-limited rate constants of reactions between *neutral* molecules.[5]

$$k_{\text{diff}} = 8000RT/3\eta \qquad (2)$$

where η is viscosity (Pa s), R is the gas constant, and T is the absolute temperature. In the case of the ionic liquids there is a significant change in the reaction rate with salt addition under low-viscosity conditions ($0.5 < \eta < 1$ mPa s). The solution viscosities barely increased upon addition of the ionic liquids up to almost 1 M, while greater screening of the electrostatic repulsion between diiodide anions caused the reaction rate constants to increase over one order of magnitude from 3×10^8 to 5×10^9 $M^{-1}\,s^{-1}$. However, at higher viscosities ($\eta > 2$ mPa s), there was no further increase of the reaction rates, which remained close to the behavior of the diffusion-limited rate constant as predicted by eq 2. This transition represents a change in regimes between a methanol solution of a salt and an ionic liquid containing methanol as a cosolvent. The behavior shown in Figure 2 indicates that the diffusion coefficients of the diiodide anions in the ionic liquid/methanol mixtures follow those of the constituent ions of the ionic liquid.

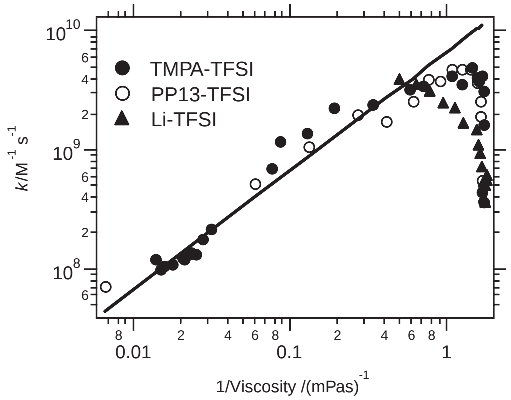

Figure 3. Plots of rate constants for reaction between I_2^- anion radicals as a function of the inverse of viscosity: Filled circle, TMPA–TFSA; open-circle, PP13–TFSA; filled triangle, Li–TFSA.

For the Li–TFSA salt, in the lowest viscosity region ($\eta < 0.7$ mPa s) there is no significant difference between Li–TFSA and the ionic liquids. However, at a slightly higher viscosity region ($0.7 < \eta < 2.0$ mPa s), the viscosity dependence of the reaction rate is different from that for the ionic liquids. At the same viscosity level, the reaction rate for the Li–TFSA solution is slower than those for the ionic liquid salts. As the reaction rate constant is very close to the diffusion limit for neutral molecules calculated from eq 2 at $\eta = 2.0$ mPa s, it can be said that the electrostatic repulsion between I_2^- anions is almost entirely screened by Li–TFSA at this concentration.

In conclusion, it is found that the ionic liquids TMPA–TFSA and PP13–TFSA can effectively screen the Coulombic repulsion between I_2^- anions than the inorganic salt Li–TFSA in methanol. At higher concentrations of the ionic liquids the reaction rates decrease owing to increasing viscosities.

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References

1 C. Nanjundiah, S. F. McDevitt, V. R. Koch, *J. Electrochem. Soc.* **1997**, *144*, 3392.
2 D. R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, *J. Phys. Chem. B* **1999**, *103*, 4164.
3 A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* **2003**, *107*, 4024.
4 P. Wang, S. M. Zakeeruddin, J. E. Moser, R. Humphry-Baker, M. Grätzel, *J. Am. Chem. Soc.* **2004**, *126*, 7164.
5 K. Takahashi, S. Sakai, H. Tezuka, Y. Hiejima, Y. Katsumura, M. Watanabe, *J. Phys. Chem. B* **2007**, *111*, 4807.
6 R. Kawano, M. Watanabe, *Chem. Commun.* **2005**, 2107.
7 K. H. Schmidt, D. M. Bartels, *Chem. Phys.* **1995**, *190*, 145.

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