Diffusion-Controlled Electron-Transfer Reactions in Ionic Liquids

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The reactions of pyridinyl and alkylpyridinyl radicals with duroquinone involve an electron transfer to produce the durosemiquinone radical in a diffusion-controlled process. The rate constants for such reactions in several ionic liquids and molecular organic solvents are determined by pulse radiolysis. The ionic liquids used are *N*-butylpyridinium tetrafluoroborate ($BuPyBF_4$) and the following tetraalkylammonium (R_4N^+) salts of bis-(trifluoromethylsulfonyl)imide ($^-NTf_2$): methyltributylammonium ($MeBu_3NNTf_2$), hexyltributylammonium ($HxBu_3NNTf_2$), methyltrioctylammonium ($MeOc_3NNTf_2$), and methylbutylpyrrolidinium ($MeBuPyrNTf_2$). The molecular solvents used are triethanolamine (TEOA) and cyclohexanol (*c*-HxOH). The experimental rate constants in the molecular solvents are only slightly higher than the diffusion-controlled rate constants estimated from the viscosity. On the other hand, the experimental values in the ionic liquids are about an order of magnitude higher than the values estimated from the measured viscosity. The reason for this difference is suggested to be due to the voids that exist in ionic liquids and the possibility that diffusion of reacting species takes place through movement of segments of the ions while the viscosity is related to movement of the whole ions.

Introduction

Room-temperature ionic liquids[1] have been proposed as solvents for green processing because they are nonvolatile and nonflammable, can dissolve different types of compounds simultaneously, and their physical properties may be tuned by varying the structures of their ions. To understand the effects of ionic liquids on chemical reactions, the rate constants for several elementary reactions in ionic liquids have been studied[2] by the pulse radiolysis technique and compared with those in other solvents. In many cases the rate constants in ionic liquids were lower than those in water and common organic solvents. For diffusion-controlled reactions, the lower rate constants in ionic liquids were clearly due to their high viscosity.[2b] It was assumed that the diffusion-controlled limit can be estimated from eq 1, which is commonly used for molecular solvents.

$$k_{\mathrm{diff}} = 8000RT/3\eta \qquad (1)$$

For the ionic liquid *N*-butylpyridinium tetrafluoroborate ($BuPyBF_4$) the viscosity was measured to be $\eta = 0.14$ Pa s and thus $k_{\mathrm{diff}} = 5 \times 10^7$ L mol^{-1} s^{-1} was estimated. However, the rate constants for electron transfer from the *N*-butylpyridinyl radical ($BuPy^\bullet$) to methyl viologen, 4-nitrobenzoic acid, and duroquinone (DQ) were measured to be considerably higher than this estimated limit.[2b]

$$BuPy^\bullet + DQ \rightarrow BuPy^+ + DQ^{\bullet -} \qquad (2)$$

Since the $BuPy^\bullet$ radical is derived from the solvent cation by one-electron reduction, it was speculated that the increased rate of reaction was due to electron hopping through solvent cations.[2b] More recent studies, however, found experimental rate constants that are higher than the diffusion limit estimated from the viscosity for reactions that cannot involve such a mechanism, i.e., quenching of triplet benzophenone by naphthalene[3] and reaction of the solvated electron with aromatic compounds.[4] Therefore, it was decided to measure the rate constant for reaction 2 under conditions that the solvent is not solely $BuPyBF_4$ but a mixture of this with other ionic liquids or molecular solvents. The results indicate that the experimental rate constants in molecular solvents are only slightly higher that those predicted from the viscosity, whereas the experimental values in ionic liquids are much higher than the predicted values.

Experimental Section[5]

The ionic liquids *N*-butylpyridinium tetrafluoroborate ($BuPyBF_4$) and methyltributylammonium bis(trifluoromethylsulfonyl)imide ($MeBu_3NNTf_2$) were prepared as described before.[2b] *N*-Methyl-*N*-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($MeBuPyrNTf_2$) was prepared by a method similar to that described before.[6] *N*-Methylpyrrolidine (1 mol) and 1-bromobutane (1.1 mol) in anhydrous EtOH (130 mL) were refluxed for 4 h to 5 h with continuous stirring. After cooling, the solvent and excess of 1-bromobutane were removed in a rotary evaporator under vacuum at 70 °C and the *N*-methyl-*N*-butylpyrrolidinium bromide product was recrystallized with acetone/methanol, filtered and washed with cool acetone, taking care to avoid exposure of the hygroscopic product to humidity. The remaining liquid contained additional amounts of the product, which were recovered after evaporation and recrystallized in the same manner. The total yield after recrystallization was 66%. This bromide salt was converted into the ionic liquid by metathesis with lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$) in water, as described for $MeBu_3NNTf_2$,[2b] washed 6 times with water to remove LiBr and unreacted compounds, and dried in a vacuum at 80 °C.

Hexyltributylammonium bis(trifluoromethylsulfonyl)imide ($HxBu_3NNTf_2$) was prepared by a similar method. Tributylamine

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(0.1 mol) and 1-bromohexane (0.11 mol) in 150 mL of anhydrous EtOH were refluxed for 48 h with continuous stirring. After cooling, the solvent and excess 1-bromohexane were removed in a rotary evaporator under vacuum at 80 °C to produce a yellow solution of hexyltributylammonium bromide containing small amounts of unreacted tributylamine, which could not be removed by extraction. The yellow product was dissolved in water (100 mL) and passed through activated carbon. The resulting colorless solution was ion-exchanged into hexyltributylammonium hydroxide, the remaining tributylamine was removed by extraction with dichloromethane, and the hydroxide was then converted into the ionic liquid by metathesis with $LiNTf_2$, washed 6 times with water, and dried.

Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($MeOc_3NNTf_2$) was prepared from the commercial chloride salt, Aliquat 336 (Aldrich), which contains a mixture of octyl and decyl chains, with predominantly octyl chains. The light orange commercial liquid was mixed with EtOH and passed through a column of activated carbon until it became colorless. Evaporation of the alcohol in a rotary evaporator and then drying in a vacuum at 80 °C produced a white solid. This chloride salt was dissolved in water and mixed with an equimolar amount of $LiNTf_2$. The ionic liquid was separated, washed 6 times with water, and then dried in a vacuum at 80 °C. Although it is named methyltrioctyl, it does contain a small unknown fraction of decyl chains.

Cyclohexanol (*c*-HxOH) was Reagent Grade from Fisher, triethanolamine (TEOA) was Baker Analyzed Reagent, and all the other solvents and starting materials for the syntheses were of the purest grade available from Aldrich.[5] Water was purified with a Millipore[5] Super-Q system.

Fresh solutions were prepared containing various concentrations of duroquinone in a solvent mixture composed of an ionic liquid or molecular solvent along with $BuPyBF_4$ as the source of the $BuPy^\bullet$ radicals. In *c*-HxOH it was not possible to dissolve sufficient $BuPyBF_4$ (or other pyridinium salts) and we have used pyridine instead. Solvated and dry electrons produced by the radiolysis react rapidly with the butylpyridinium cation to produce the $BuPy^\bullet$ radical.[2b]

$$e^- + BuPy^+ \rightarrow BuPy^\bullet \tag{3}$$

Electrons also react rapidly with pyridine[7] to produce a radical anion, which undergoes very rapid protonation to form the $HPy^\bullet$ radical.[8]

$$e^- + Py \rightarrow Py^{\bullet -} \tag{4}$$

$$Py^{\bullet -} + ROH \rightarrow HPy^\bullet + RO^- \tag{5}$$

Rate constants for reaction 2 and for the similar reaction involving $HPy^\bullet$ were determined by pulse radiolysis using (0.1 to 1.5) μs pulses of 6 MeV electrons from a Varian linear accelerator and following the formation of the durosemiquinone optical absorption at 440 nm; other details were as described before.[9] The dose per pulse was determined by thiocyanate dosimetry.[10] The measurements were performed at room temperature, (22 ± 2) °C. Rate constants are reported with their estimated standard uncertainties, which include the standard deviation of the kinetic fits and estimated uncertainties in the concentrations.

Viscosity measurements of the irradiated mixtures were carried out at 24 °C in steady shear between a 40 mm diameter plate and a 40 mm diameter cone with an angle of 0.04 rad and a gap of <0.1 mm, using a Rheometric Scientific, Inc. SR-5000 rheometer.[5] Tests were performed at shear rates between 1 s^{-1} and 100 s^{-1} (referenced to the outer radius of the plates), and none of the fluids tested showed any signs of non-Newtonian behavior. The reported viscosity is the mean of 6 to 11 values determined at different shear rates, and the relative standard uncertainty of the mean viscosity was less than 5%.

Results and Discussion

Reaction 2 was chosen as a representative electron-transfer reaction between two neutral reactants that is expected to take place with a diffusion-controlled rate constant in most solvents. The reduction potential of the $DQ/DQ^{\bullet -}$ couple is −0.24 V vs NHE in aqueous solutions.[11] The reduction potential of the $BuPy^+/BuPy^\bullet$ couple in water is unknown but is expected to be more negative than the value of −0.94 V reported for NAD^+ and 1-methylnicotinamide.[11] Thus, the driving force for reaction 2 in aqueous solutions is >0.7 V. With such a high driving force, the high self-exchange rate for $DQ/DQ^{\bullet -}$ ($\approx 10^8$ L mol^{-1} s^{-1} in water and organic solvents),[12] and since pyridinyl radicals are also known to engage in very rapid electron-transfer reactions, reaction 2 is expected to be diffusion-controlled in aqueous solutions. In organic solvents and ionic liquids, the driving force of the reaction is expected to be somewhat smaller than that in water because the solvation energies of the charged products are expected to be lower. The reduction potentials of duroquinone and *N*-methylpyridinium iodide in acetonitrile are −0.84 and −1.21 V vs SCE, respectively,[13] i.e., the difference is reduced to ≈0.4 V. From our results, it appears that reaction 2 is diffusion-controlled in all solvents examined.

In the previous study,[2b] the rate constant for reaction 2 was measured in the neat ionic liquid, $BuPyBF_4$, as well as in water and 2-PrOH solutions, where a small fraction of the ionic liquid was used as the source of radicals. By assuming that the viscosities of the solutions were the same as those of the neat solvents, using the viscosity values given in the literature, and calculating k_{diff} from eq 1, it was found that the experimental rate constants in water (3.1×10^9 L mol^{-1} s^{-1}) and 2-PrOH (1.3×10^9 L mol^{-1} s^{-1}) were approximately half the estimated values of k_{diff}. In contrast, the experimental rate constant for reaction 2 in $BuPyBF_4$ (4.4×10^8 L mol^{-1} s^{-1}) was an order of magnitude higher than k_{diff} estimated from the viscosity. The latter result led to a speculation of electron hopping through solvent cations.

In the present study the rate constants were measured in mixtures of $BuPyBF_4$ with other ionic liquids and organic solvents. Samples of kinetic plots are shown in Figure 1 and the results are summarized in Table 1. In the three mixtures of $BuPyBF_4$ with $MeBu_3NNTf_2$, the rate constant decreases with decreasing fraction of the former ionic liquid. These results may be due to the increase in the viscosity of the medium and a decrease in the probability of electron hopping. In the mixtures containing only small fractions of $BuPyBF_4$, the hopping mechanism may be ruled out. Nevertheless, the experimental rate constants are about 8 times higher than the values of k_{diff} estimated from the measured viscosities (Table 1). When $MeBu_3NNTf_2$ was replaced with the more viscous $HxBu_3NNTf_2$ and $MeOc_3NNTf_2$, the ratio k_{exp}/k_{diff} increased to 11 and 13, respectively, and when it was replaced with the less viscous $MeBuPyrNTf_2$ the ratio decreased to 5. In contrast, the ratios in the molecular solvents TEOA and *c*-HxOH were both only slightly above 1 despite the wide difference in viscosity, with the TEOA solution having a measured viscosity near the upper range of the ionic liquid mixtures and *c*-HxOH having a

TABLE 1: Rate Constants for Electron Transfer from Pyridinyl Radical to Duroquinone in Different Media

medium[a]	k_{exp}[b]	η[c]	k_{diff}[d]	k_{exp}/k_{diff}
$BuPyBF_4$[e]	$(4.4 \pm 0.7) \times 10^8$	0.14	4.7×10^7	9.4
$MeBu_3NNTf_2/BuPyBF_4$ (2.1)	$(1.9 \pm 0.3) \times 10^8$	0.354	1.9×10^7	10.0
$MeBu_3NNTf_2/BuPyBF_4$ (8.9)	$(1.0 \pm 0.2) \times 10^8$	0.509	1.3×10^7	7.7
$MeBu_3NNTf_2/BuPyBF_4$ (41)	$(8.6 \pm 1.3) \times 10^7$	0.573	1.1×10^7	7.8
$HxBu_3NNTf_2/BuPyBF_4$ (14.6)	$(1.1 \pm 0.2) \times 10^8$	0.663	9.9×10^6	11.0
$MeOc_3NNTf_2/BuPyBF_4$ (12)	$(1.6 \pm 0.3) \times 10^8$	0.556	1.2×10^7	13.3
$MeBuPyrNTf_2/BuPyBF_4$ (14.6)	$(4.1 \pm 0.7) \times 10^8$	0.082	8.0×10^7	5.1
$TEOA/BuPyBF_4$ (11.5)	$(1.6 \pm 0.3) \times 10^7$	0.532	1.3×10^7	1.2
c-HxOH/Py (99)	$(2.4 \pm 0.4) \times 10^8$	0.041[f]	1.6×10^8	1.5[g]
$2\text{-}PrOH/BuPicPF_6$ (99)[e]	$(1.3 \pm 0.3) \times 10^9$	0.0022[h]	3.0×10^9	0.43
$H_2O/t\text{-}BuOH/BuPyBF_4$ (50)[e]	$(3.1 \pm 0.5) \times 10^9$	0.00108[i]	6.1×10^9	0.51

[a] The second solvent was used as the source of pyridinyl radicals, the values in parentheses are w/w ratios between the first and second solvent. [b] Experimental rate constant, in L mol^{-1} s^{-1}. [c] Viscosity, in Pa s, of the irradiated mixture measured in this work, except for the last three values. [d] Diffusion-controlled rate constant calculated from the viscosity. [e] Results from ref 2b. [f] The viscosity of neat cyclohexanol from Lange's Handbook of Chemistry; the value for the mixture with pyridine is expected to be slightly lower. [g] Since the viscosity is expected to be slightly lower, this value is expected to be correspondingly lower. [h] The viscosity of neat 2-PrOH from Viswanath, D. S.; Natarajan, G. *Data Book on the Viscosity of Liquids*; Hemisphere Publishing: New York, 1989. [i] The viscosity of aqueous *t*-BuOH (2%) solution estimated from Herskovits, T. T.; Kelly, T. M. *J. Phys. Chem.* **1973**, *77*, 381.

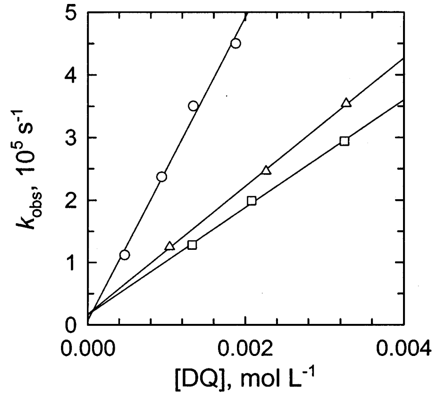

Figure 1. First-order rate constant for formation of $DQ^{\bullet-}$ at 440 nm as a function of the concentration of duroquinone in cyclohexanol (○), $BuPyBF_4/MeBu_3NNTf_2$ (1/8.9) (△), and $BuPyBF_4/MeBu_3NNTf_2$ (1/41) (□).

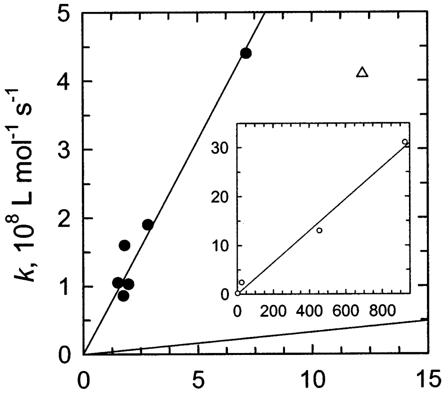

Figure 2. Dependence of the rate constant for reaction 2 on the viscosity of the medium. The solid circles are for the ionic liquids except $MeBuPyrNTf_2$, which is given by the open triangle. The insert is for the molecular solvents. The slope of the line in the insert is also given as the lower line in the main figure.

viscosity near that of the ionic liquid mixture with the lowest viscosity. This comparison suggests that, although eq 1 gives a reasonable estimate of k_{diff} in molecular solvents,[14] it underestimates k_{diff} in ionic liquids by as much as an order of magnitude or more. Graphic representation of k_{exp} vs the reciprocal viscosity ($1/\eta$) (Figure 2) shows a reasonable line for the ionic liquids (solid circles) for which the ratio k_{exp}/k_{diff} is near 10, with the deviations due to the differences discussed above. The value for $MeBuPyrNTf_2$ (triangle) shows a strong deviation from this line. The values for the molecular solvents measured in this study and in the previous study are also fit with a straight line (insert), but the slope of this line is about 20 times lower than that for the ionic liquids.

Reaction 2 involves the reaction of two neutral reactants to produce two charged products. The cation $BuPy^+$ is stable, whereas the radical anion $DQ^{\bullet-}$ may subsequently equilibrate with its protonated form $DQH^{\bullet}$. Electron transfer reactions in general take place more slowly in solvents of lower polarity, and ionic liquids have been found to behave as solvents of lower polarity than water, closer to ethanol or acetonitrile, as suggested from solvatochromic measurements.[1,15] Electron-transfer reactions may be affected by the solvent also through the change in energy of solvation of the charged species, which may affect the driving force of the reaction. In this respect, ionic liquids behave like organic solvents, with the energy of solvation of small ions being lower than that in water and alcohols.[2e] These effects can only decrease the rate constant of reaction 2 in ionic liquids and cannot explain the finding that the values are much higher than k_{diff}. It is suggested, therefore, that the viscosity of the liquid, which represents the diffusion of whole molecules or ions, does not adequately represent the diffusion of reactants within ionic liquids. This conclusion is in line with previous findings on the reactions of solvated electrons with aromatic compounds[4] and on the quenching of triplet benzophenone by naphthalene,[3] where the experimental rate constants were higher than those estimated from the viscosity.

Experimental rate constants for diffusion-controlled reactions higher than predicted from eq 1 have been observed also with polymer matrixes.[16] The effect was ascribed to the difference between the measured "macroviscosity" of the medium and the "microviscosity" in the immediate surroundings of the reactants. It was suggested that rapid movement of flexible aliphatic chains enables rapid diffusion of small reactants without diffusion of whole polymer molecules. As suggested before,[4] the situation in ionic liquids is somewhat similar. First, these salts are liquid because their large anions and cations cannot form an ordered crystal and must contain voids that can accommodate small solute molecules. Second, the butyl, hexyl, and octyl chains are flexible and can move more rapidly than the whole cation, which permits rapid diffusion of solutes from one void to another. In support of these suggestions it is found that, while the ratio k_{exp}/k_{diff} is about 8 with the $MeBu_3N^+$ cation, it is 11 and 13 with the progressively larger and more flexible $HxBu_3N^+$ and $MeOc_3N^+$ cations, but only 5 with the more compact and less flexible $MeBuPyr^+$ cation.

Since the actual diffusion-controlled limit in ionic liquids is higher than k_{diff} estimated from the viscosity by a factor of 5 to 13, we should reconsider previous results where measured rate constants were compared to k_{diff}. In the oxidation of chlorpromazine and Trolox by the $CCl_3O_2^\bullet$ radical in ionic liquids (Table 4 in ref 2b) the measured rate constants were lower than k_{diff} by a factor of 2 to 10 and were corrected for the effect of the diffusion limit to derive the activation-controlled rate constants. Since the diffusion limit is much higher than the values of k_{diff} estimated from the viscosity, those corrections will be much smaller. For practical purposes, the uncorrected values for the rate constants and activation energies may be used. This change, however, does not alter the conclusions drawn from those results.[2b] In the same study, the rate constant for electron transfer from benzophenone ketyl radical to duroquinone in the ionic liquid $MeBu_3NNTf_2$ was compared to the values in 2-PrOH, aqueous 2-PrOH, and glycerol (Table 1 in ref 2b). It was assumed that the value in the ionic liquid was diffusion-controlled, similar to the situation in aqueous and glycerol solutions and different from the case of 2-PrOH. The conclusions from the present study suggest, however, that that value is significantly lower than the diffusion-controlled limit. Therefore, the finding (Table 1 in ref 2b) that the rate constant for this electron-transfer reaction decreases by an order of magnitude upon going from aqueous to 2-PrOH solutions and again by another order of magnitude upon going to the ionic liquid solution is a real effect of the ionic liquid on the rate of reaction and is not due to the limiting effect of diffusion.

In summary, diffusion-controlled rate constants in ionic liquids are significantly higher than the values predicted from the measured viscosity on the basis of eq 1. The extent of increase is approximately an order of magnitude and varies with the structure of the ionic liquid. In the present study, the increase was by a factor of 5 for an ionic liquid with a compact cation and becomes larger (up to 13) as the length and flexibility of the aliphatic chains increase. This effect is expected to depend also on the size of the reacting species so that very small molecules and radicals may react in viscous ionic liquids nearly as rapidly as in water and classical organic solvents.

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References and Notes

(1) Wasserscheid, P.; Welton, T. (Eds.) *Ionic Liquids in Synthesis*; Wiley-VCH: New York, 2002. Brennecke, J. F.; Maginn, E. J. *AIChE J.* **2001**, *47*, 2384.

(2) (a) Behar, D.; Gonzalez, C.; Neta, P. *J. Phys. Chem. A* **2001**, *105*, 7607. (b) Behar, D.; Neta, P.; Schultheisz, C. *J. Phys. Chem. A* **2002**, *106*, 3139. (c) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 5468. (d) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 9030. (e) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 11130.

(3) McLean, A. J.; Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *Chem. Commun.* **2002**, 1880.

(4) Wishart, J. F.; Neta, P. *J. Phys. Chem. B* **2003**, *107*, 7261.

(5) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

(6) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B* **1999**, *103*, 4164.

(7) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513. NDRL/NIST Solution Kinetics Database, NIST Standard Reference Database 40, 1995. http://kinetics.nist.gov/solution/index.php.

(8) Cercek, B.; Ebert, M. *Trans. Faraday Soc.* **1967**, *63*, 1687. Simic, M.; Ebert, M. *Int. J. Radiat. Phys. Chem.* **1971**, *3*, 259. Fessenden, R. W.; Neta, P. *Chem. Phys. Lett.* **1973**, *18*, 14.

(9) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2000**, *104*, 4475.

(10) Schuler, R. H.; Patterson, L. K.; Janata, E. *J. Phys. Chem.* **1980**, *84*, 2088.

(11) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(12) Meisel, D.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 7505. Fukuzumi, S.; Nakanishi, I.; Suenobu, T.; Kadish, K. M. *J. Am. Chem. Soc.* **1999**, *121*, 3468. Layloff, T.; Miller, T.; Adams, R. N.; Fah, H.; Horsfield, A.; Proctor, W. *Nature (London)* **1965**, *205*, 382.

(13) Meites, L.; Zuman, P. *CRC Handbook Series in Organic Electrochemistry;* CRC Press: Boca Raton, FL, 1977−1982; Volume I−V.

(14) The values of k_{diff} estimated from the viscosity by using eq 1 are considered to be lower limits and may be higher by up to 50% depending on the exact shapes of the reactants (Edwards, J. T. *J. Chem. Educ.* **1970**, *47*, 261).

(15) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591. Aki, S. N. V. K.; Brennecke, J. F.; Samanta, A. *J. Chem. Soc., Chem. Commun.* **2001**, 413. Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *J. Chem. Soc., Perkin Trans. 2* **2001**, 433.

(16) Chu, D. Y.; Thomas, J. K. *J. Phys. Chem.* **1989**, *93*, 6250. *Macromolecules* **1990**, *23*, 2217.