

Molar absorption coefficient and radiolytic yield of solvated electrons in diethylmethyl(2-methoxy)ammonium bis (trifluoromethanesulfonyl)imide ionic liquid

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Abstract

The molar absorption coefficient and the radiolytic yield of solvated electron in ionic liquid of DEMMA-TFSI were estimated respectively to be $2.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.8 \times 10^{-7} \text{ mol J}^{-1}$ by observing the reaction and kinetics of solvated electron and dry electron in the ionic liquid. The solvated electron in DEMMA-TFSI has a very broad absorption spectrum peaking at 1100 nm and reacts slowly with pyrene with a rate constant of $3.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, while the dry electron is captured rapidly by pyrene with C_{37} value of 0.065 mol L^{-1} .

Keywords: Ionic liquid, Solvated electron, Dry electron, Molar absorption coefficient, Radiolytic yield, Pulse radiolysis

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1. Introduction

Room temperature ionic liquids, novel green recyclable, have gained a great deal of attention as a new class of compounds for replacement of conventional organic solvents due to their unique properties, i.e. negligible volatility, thermal and chemical stability, and so on. Therefore, the ionic liquids have been proposed for applications in various fields such as organic chemical reactions, catalysis, extractions and electrochemistry (Welton, 1999; Wasserscheid and Keim, 2000; Sheldon, 2001; Funston *et al.*, 2007). Recently, the ionic liquids have aroused much interest as new media in nuclear fuel reprocessing (Shkrob *et al.*, 2007). The ionic liquid is also an interesting solvent for studying radiation chemistry, such as reaction and kinetics of solvated electrons and dry electrons, electron transfer, and so on, because of the existence of free cation and anion at room temperature.

Several pulse radiolysis studies on ionic liquids (Behar *et al.*, 2001; Behar *et al.*, 2002; Grodkowski and Neta, 2002a-c; Wishart and Neta, 2003; Grodkowski *et al.*, 2003; Wishart *et al.*, 2005; Kato, *et al.*, 2007; Takahashi *et al.*, 2007; Kimura *et al.*, 2007) have been reported. The researches indicate that, for the imidazolium ionic liquids, dry electrons produced by ionization before full solvation are rapidly scavenged by the solvent molecules. In the ammonium ionic liquids, the electrons are solvated quickly to form solvated electrons. The solvated electrons in the ammonium ionic liquids have a very broad absorption band peaking over 1000 nm. In R_4NNTf_2 (Wishart and Neta, 2003), a radiolytic yield of the solvated electrons was observed to be 0.7×10^{-7} mol J^{-1} in the nanosecond time region and the peak molar absorption coefficient of the solvated electron was reported to be 2.2×10^4 L mol^{-1} cm^{-1} at 1410 nm. The reactions of the solvated electrons with some aromatic scavengers such as benzophenone and pyrene are diffusion-limited, with rate constants in order of 10^8 L mol^{-1} s^{-1} . Moreover, the radiolysis studies indicate that the dry electron capture with scavengers is very efficient in ionic liquids. However, the study on the primary processes or reactions in ionic liquids (e.g. reaction of solvated electron and dry electron) and the estimation of the initial yields of the solvated electrons or species are essential in order to design the ionic liquids for new applications.

We have, therefore, proposed femto-, pico- and nanosecond pulse radiolysis to observe the dynamics of solvated electron and dry electron in ionic liquids. The present work reports the spectrum, the molar absorption coefficient, and the radiolytic yield of solvated electrons in ionic liquid of N,N-Diethyl-n-methyl-n-(2-methoxy)ammonium bis (trifluoromethanesulfonyl)imide (DEMMA-TFSI) based on the nanosecond pulse radiolysis studies. The reaction and kinetics of solvated electron and dry electron with pyrene solute in DEMMA-TFSI were observed.

2. Experimental

In the present work, a hydrophobic ionic liquid of N,N-Diethyl-n-methyl-n-(2-methoxy) ammonium bis(trifluoromethanesulfonyl)imide (DEMMA-TFSI; produced by Kanto Chemical Co.,

the viscosity of 120 mPa s at 20°C) was used. Before the experiment, the ionic liquid was purified by repeated extractions with water (4 times) to remove LiCl and excess reagent, and then dried three hours under vacuum at 80°C.

The optical absorption spectrum and transient absorption time profile were measured by Osaka University nanosecond pulse facility based on an 8 ns electron pulse from a 28 MeV L-band linear accelerator. Analyzing light was provided by a pulsed xenon flash lamp. A monochromator with narrow (10 nm) band-pass filters was used to select the analyzing light wavelength. The transient absorption signals were measured by a silicon photodiode at wavelength of ≤ 1000 nm and an InGaAs photodiode at ≥ 1000 nm. All measurements were carried out at room temperature. A 10-mm-thick sample cell and a radiolytic dose of around 21 Gy were used in the transient absorption measurement.

3. Results and Discussion

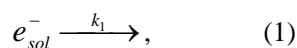
3.1. Spectra of solvated electrons in DEMMA-TFSI

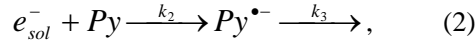
Figure 1 shows the optical absorption spectra of solvated electrons obtained in the nanosecond pulse radiolysis of DEMMA-TFSI with 0 and 16 mmol L⁻¹ pyrene. The solvated electron in DEMMA-TFSI has a very broad absorption band peaking at 1100 nm, i.e. 1.1eV with energy band width of 0.6 eV in full-width at half-maximum (FWHM). The electrons in DEMMA-TFSI can be considered to be weakly solvated, similar to ionic liquids of TMPA-TFSI (Katoh *et al.*, 2007), P13-TFSI and P14-TFSI (Takahashi *et al.*, 2007), but is stronger than ionic liquid of R₄NNTf₂ (1410 nm) (Wishart and Neta, 2003). By adding the pyrene solute, the solvated electrons react with pyrene to produce pyrene anion radicals, resulting in the decrease of the optical density at 1100 nm and the increase at around 480 nm. The absorption band around 1100 nm in Fig. 1 is, therefore, assigned to the solvated electrons. The small absorption band that peaks at 440 nm is assigned to the pyrene cation radical produced by the reaction of the solvent cation radical with pyrene.

3.2. Yield and reactions of solvated electrons

Figures 2 and 3 show respectively the solvated electron decay in DEMMA-TFSI at 1100 nm and the formation of pyrene anion radical at 480 nm as functions of the pyrene concentration. In the case of the absence of solute, the solvated electron decays via a simple first-order process with a rate constant of $k_1 = 6.4 \times 10^6$ s⁻¹ (lifetime: 160 ns). The relative short lifetime suggests that the solvated electrons react with some solvent molecules in ionic liquid. However, it must be reacting with impurities or the residual water rather than through a second-order process with a hole species.

The reaction of the solvated electrons with pyrene solute is dependent on the concentration of pyrene,





where e_{sol}^- , Py , and $Py^{\bullet-}$ represent the solvated electron, the pyrene, and the pyrene anion radical, respectively. The decay rate of the solvated electron in the ionic liquid increases with the pyrene concentration, while the yield of pyrene anion radical formed increases with the pyrene concentration. The decrease of the initial solvated electron yield in Fig. 2(a) and the increase of the initial pyrene anion radical yield in Fig. 3 are due to the reaction of the dry electron with pyrene, as described below. The first-order rate constants calculated from the solvated electron decay show a linear correlation with the pyrene concentration, as given in Fig. 2(b). The second-order rate constant of the solvated electron reaction with pyrene is obtained to be $k_2 = 3.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. The observed rate constant is lower than that in water and alcohols by 2 orders of magnitude. According to the diffusion theory because of the viscosity of DEMME-TFSI being over 2 orders of magnitude higher than that of water and alcohols, the reaction of the solvated electrons with pyrene is also diffusion limited. However, the diffusion-controlled limit for DEMMA-TFSI can be estimated for the viscosity and the equation $K_{diff} = 8000RT/3\eta$ to be about $5.5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$. The observed rate constant for the reaction of the solvated electron with pyrene thus exceeds the limit by near one order of magnitude. Similar researches were also reported in several butylmethylimidazolium ionic liquids (McLean *et al.*, 2002; Skryzpczak *et al.*, 2003), R_4NNTf_2 ionic liquid (Wishart and Neta, 2003), and TMPA-TFSI ionic liquid (Katoh *et al.*, 2007).

Now, we can estimate the radiolytic yield and the molar absorption coefficient (ϵ_{sol}) of solvated electrons in ionic liquid from the rate constants of the decay and reaction of the solvated electrons, as described above, with the obtained rate constants of k_1 and k_2 as,

$$G_{sol}(t) = G_{sol}(0) \exp\{-c/C_{37} - (k_1 + k_2 c)t\}, \quad (3)$$

$$G_{Py}(t) = G_{sol}(0) \exp(-c/C_{37}) k_2 c / (k_1 + k_2 c - k_3) [\exp(-k_3 t) - \exp\{-(k_1 + k_2 c)t\}] \\ + G_{sol}(0) \{1 - \exp(c/C_{37})\} \exp(-k_3 t), \quad (4)$$

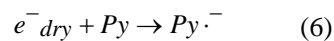
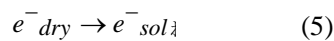
where $G_{sol}(t)$ and $G_{Py}(t)$ are the yields of the solvated electron and the pyrene anion radical at time t , $G_{sol}(0)$ and $G_{Py}(0)$ are the initial yields of the solvated electron and the pyrene anion radical at time zero, c is the concentration of pyrene in ionic liquid, $C_{37} = 0.065 \text{ mol L}^{-1}$ is the fractional yield of the solvated electrons remaining after the reaction of dry electrons, as described below. Therefore, we can fit the kinetics of the pyrene anion radicals (i.e. the formation and decay of the pyrene anion radicals as given in Fig. 3 at 480 nm) as a function given in Eq. (4). The fitting results are given as the solid lines in Fig. 3, where the rate constant of pyrene anion radical is estimated to be $k_3 = 2 \sim 3 \times 10^6 \text{ s}^{-1}$. By using the molar absorption coefficient of $5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ for pyrene anion radical (Wishart and Neta, 2003), the radiolytic yield of the solvated electrons in DEMME-TFSI was thus obtained to be $0.8 \times 10^{-7} \text{ mol J}^{-1}$ at time zero, i.e. the pulse end of electron beam (the actual time ~ 10 ns). The peak molar absorption coefficient of solvated electrons in DEMMA-TFSI was obtained to

$2.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ from the measured optical density at 1100 nm (in Fig. 2(a)). It would be noted that the molar absorption coefficient of the solvated electron in ionic liquid of DEMMA-TFSI is slightly higher than that in the polar solvents such as water, but the yield is lower than water by a factor of 4. The similar results in R_4NNTf_2 ionic liquid ($0.7 \times 10^{-7} \text{ mol J}^{-1}$ and $2.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 1410 nm) were reported by Wishart and Neta.

3. 3. Dry electron capture by pyrene.

The dry electron before full solvation is captured efficiently by pyrene solute, resulting in the initial solvated electron decreases in Fig. 2(a) and the initial pyrene anion radical increases in Fig. 3. The experimental data indicates that, comparing with the reaction of the solvated electron with pyrene, the dry electron in DEMMA-TFSI reacts rapidly with the pyrene. The rate constant of the dry electron capture with solutes can not observed within the nanosecond time region. However, the fractional yield of the solvated electrons remaining after the dry electron capture can be evaluated by using the relation $G_c/G_0 = \exp(-c/C_{37})$, where G_c is the yield of solvated electrons at a given solute concentration c , G_0 is the yield of solvated electrons without scavenger, and C_{37} is the concentration at which only 37% ($=1/e$) of the electrons survive to be solvated. Figure 4 shows plots of $\ln(G_c/G_0)$ as a function of the pyrene concentration in DEMMA-TFSI. The C_{37} value of pyrene in DEMMA-TFSI is obtained to be 0.065 mol L^{-1} . The obtained C_{37} value is comparable with previous reported values: 0.062 mol L^{-1} for benzophenone, 0.063 mol L^{-1} for pyrene, 0.084 mol L^{-1} for phenanthrene in R_4NNTf_2 (Wishart *et al.*, 2003), and 0.057 mol L^{-1} for Bmim cation in TMPA-TFSI (Katoh *et al.*, 2007).

The dry electron capture by pyrene also provides a convenient method to estimate the molar absorption coefficient and the initial radiolytic yield of the solvated electrons in DEMMA-TFSI by assuming that the dry electron only solvates to form the solvated electron or reacts with pyrene to produce pyrene anion radical,



The molar absorption coefficient of the solvated electron in DEMMA-TFSI at 1100 nm is thus obtained to be $\varepsilon_{sol} = \varepsilon_{Py} \Delta OD_{Py} / \Delta OD_{sol} = 2.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, where ΔOD_{Py} and ΔOD_{sol} , calculated from the experimental data in Figs. 3 and 2(a), are respectively the increase of optical density at 480 nm at 10 ns (the initial pyrene anion radical yield due to the dry electron reaction) and the decrease of the optical density at 1100 nm at 10 ns (decrease of the initial solvated electron yield due to the dry electron reaction with pyrene). The initial yield of the solvated electrons was estimated to be $0.8 \times 10^{-7} \text{ mol J}^{-1}$ at 10 ns. The molar absorption coefficient and the initial yield

agree with that from the analysis of the reaction of the solvated electron with pyrene. It indicates that the pulse radiolysis is a useful tool to study the ultrafast reactions and kinetics in ionic liquids.

4. Conclusion

The molar absorption coefficient and the radiolytic yield of solvated electrons in diethylmethyl (2-methoxy)ammonium bis(trifluoromethanesulfonyl)imide (DEMMA-TFSI) DEMMA-TFSI ionic liquid were estimated by observing the reaction and kinetics of solvated electron and dry electron in ionic liquid with a nanosecond pulse radiolysis technique. It is found that the solvated electron in DEMMA-TFSI has a very broad absorption spectrum peaking at 1100 nm. The electrons in ionic liquid DEMMA-TFSI is weakly solvated, similar to ionic liquids of TMPA-TFSI, P13-TFSI and P14-TFSI, but is stronger than ionic liquid of R_4NNTf_2 (1410 nm). The peak molar absorption coefficient and radiolytic yield of the solvated electrons in DEMMA-TFSI were obtained to be $2.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.8 \times 10^{-7} \text{ mol J}^{-1}$, respectively.

The reaction of the solvated electron with solute (i.e. pyrene) is found to be diffusion-controlled, with a lower rate constant of $3.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$, but the reaction of the dry electron with pyrene is very efficient with C_{37} value of 0.065 mol L^{-1} , which suggests that the electrons in DEMMA-TFSI could diffuse before full solvation. It indicates that the ionic liquid is an interesting reaction medium for examining the reaction mechanism of dry electrons. However, pico- and femtosecond time-resolved measurements should be examined for detailed knowledge of the reactions of dry electron in ionic liquids.

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Figure captions

Fig.1. Transient absorption spectra observed in the nanosecond pulse radiolysis for neat DEMMA-TFSI and that with 16 mM pyrene at time zero, i.e. the pulse end of electron beam (the actual time ~ 10 ns).

Fig.2. (a) Transient absorption kinetics of solvated electrons at 1100 nm with (top to bottom) 0, 4, 8, 12, and 16 mmol L⁻¹ pyrene in DEMMA-TFSI. Radiolytic dose: 21 Gy, and (b) Plots of observed rate constants for solvated electron decay versus pyrene concentration.

Fig. 3 Transient absorption kinetics (dots) of pyrene anion radicals at 480 nm with (bottom to top) 0, 4, 8, 12, and 16 mmol L⁻¹ pyrene in DEMMA-TFSI, radiolytic dose: 21 Gy, and the fitting results! (solid line) by Eq. (4).

Fig. 4. Plots of $\ln(G_e/G_0)$ as a function of the pyrene concentration in DEMMA-TFSI.

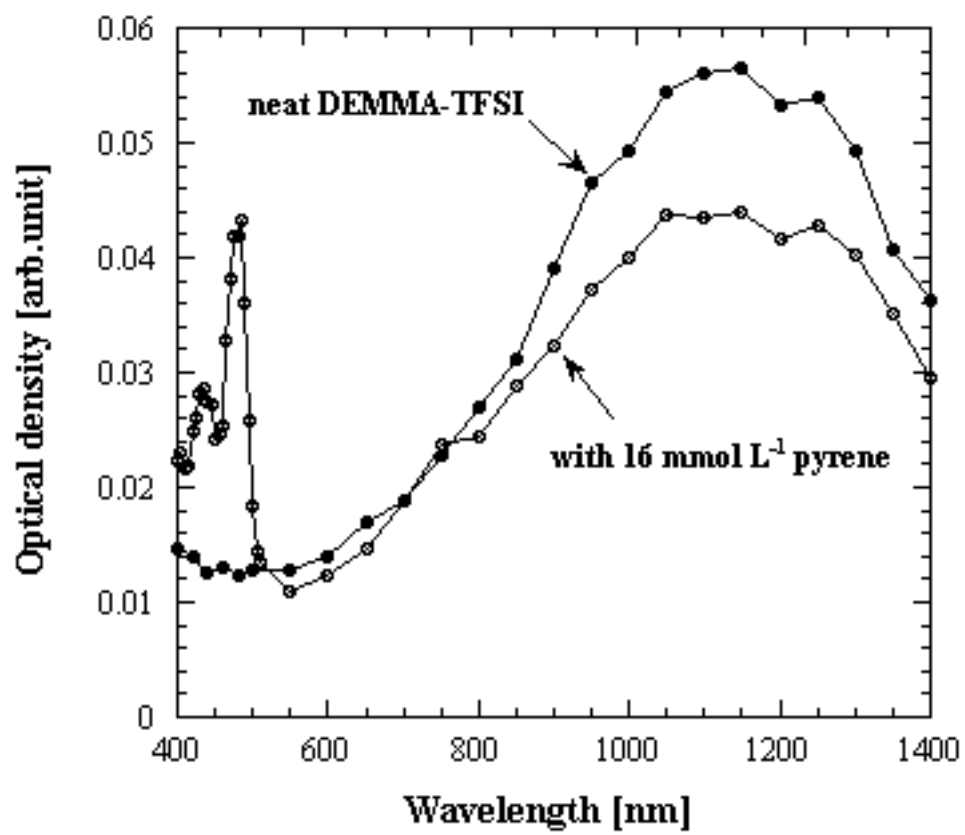


Fig. 1

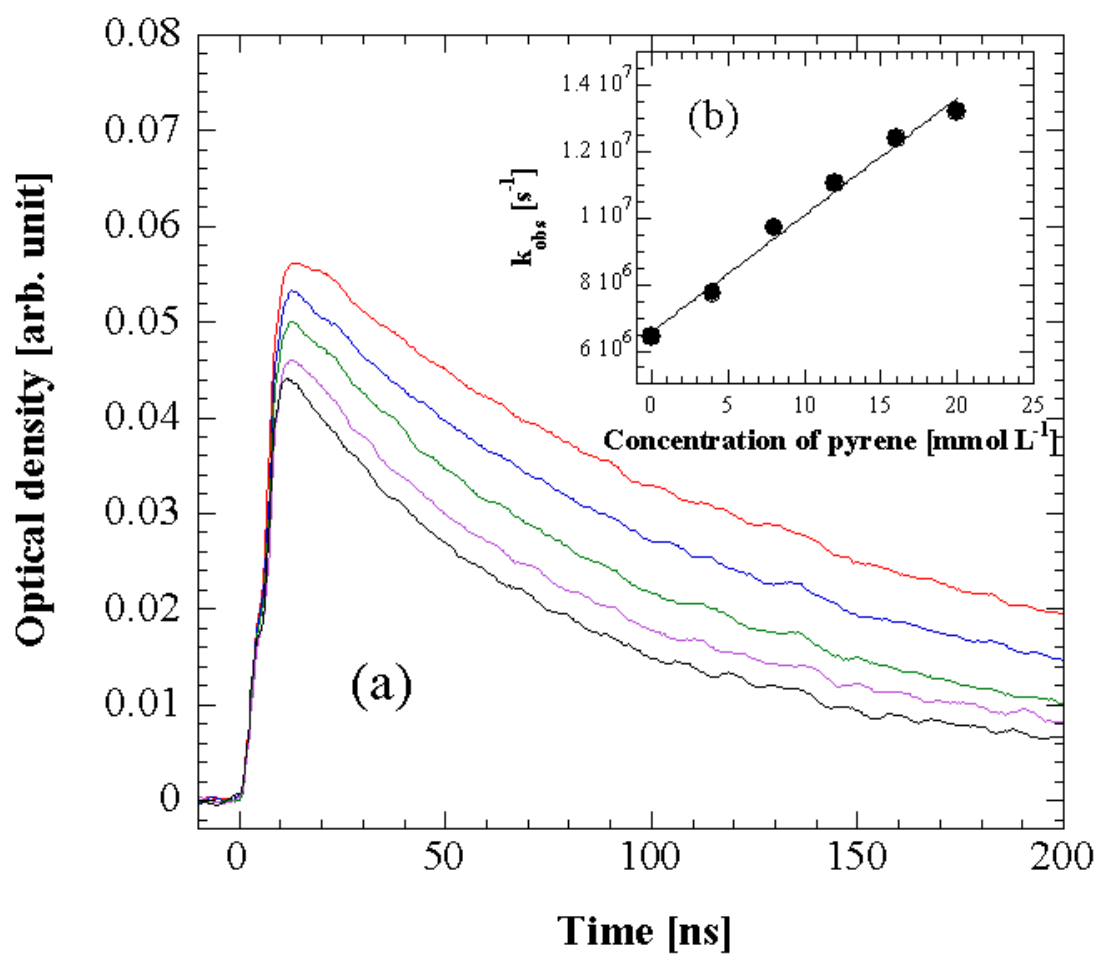


Fig. 2

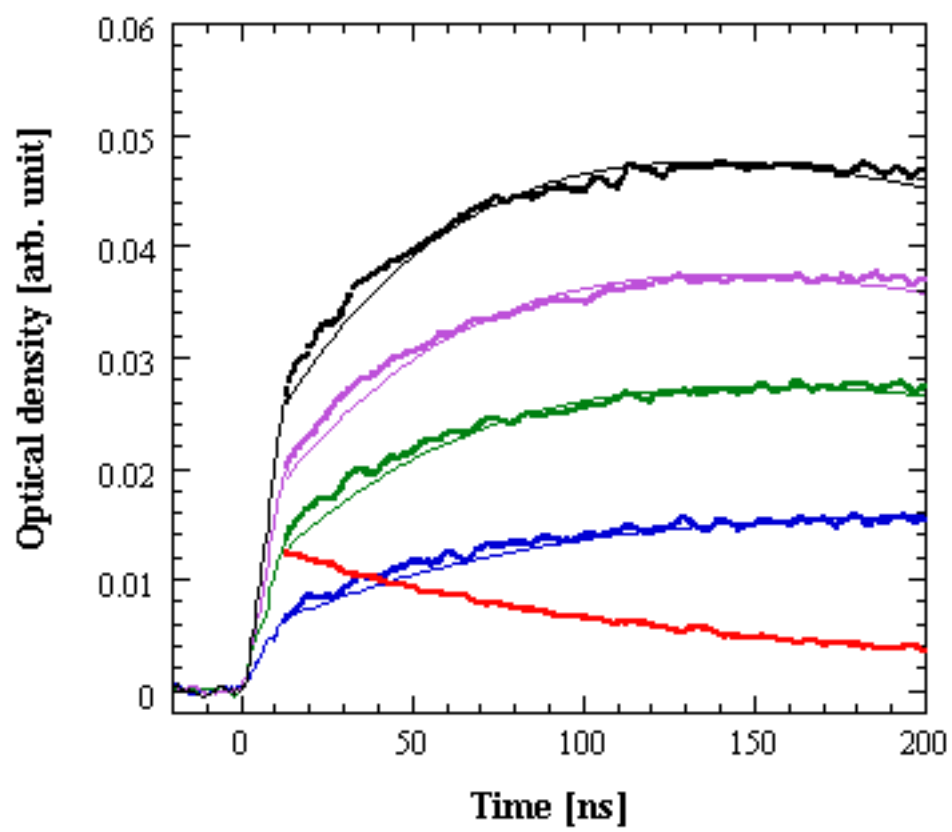


Fig. 3

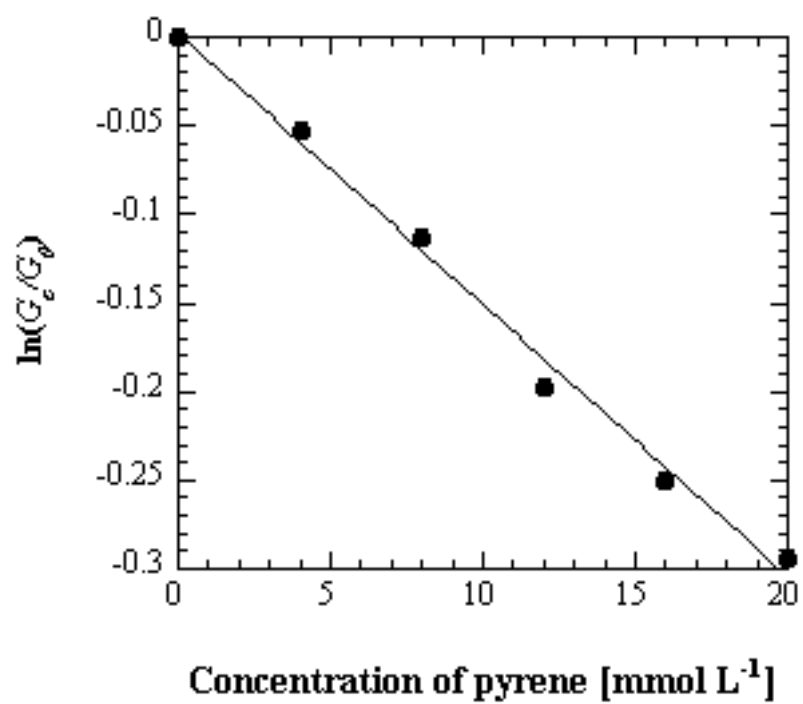


Fig. 4