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13. ABSTRACT
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Diffusion of Molecular Probes in Thermoresponsive Poly(*N*-isopropylacrylamide) Hydrogels: Electroanalytical Studies

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ABSTRACT

Poly(N-isopropylacrylamide), NIPA, thermoresponsive hydrogels with well defined concentrations of an electroactive probe, 1,1'- ferrocenedimethanol, $Fc(MeOH)_2$, were prepared. The discontinuous reversible volume phase transition of such gels occurs at 32 ± 1 °C, and results in a release of approximately 93% of the solvent from the polymeric network. Transport of $Fc(MeOH)_2$ in both swollen and collapsed gels was studied using steady state voltammetry and chronoamperometry at platinum microelectrodes. The diffusion coefficient of $Fc(MeOH)_2$ in collapsed gels was approximately two orders of magnitude smaller than that in swollen gels. UV/vis spectroscopic studies shown that for a 3.0% NIPA gel the concentration of $Fc(MeOH)_2$ in collapsed gel phase was approximately 6 time higher than that in released solution and 4.5 times higher than in the original swollen gel.

INTRODUCTION

Chemically cross-linked poly(N-isopropylacrylamide) gels, NIPA, swollen by water or an aqueous solution have been known to undergo a continuous reversible volume phase transition at approximately 34 °C [1]. This transition results in a significant change of the volume of a gel. During the past two decades, NIPA gels have been a subject of intensive interest [1-6]. The swelling behavior of NIPA gels in water and the internal structure of NIPA gels have been systematically studied. The unique properties of polymeric hydrogels such as NIPA gels are that they can contain up to 99% of water, but they also have properties of solid matter. Under certain circumstances, the liquid can be released from the gel through a discontinuous volume phase transition; this process is reversible. Thus, polymeric gels are ideal materials for leak-free liquid storage devices and controlled release matrixes. Many applications of temperature-sensitive gels have been proposed and investigated including injectable hydrogel that supports tissue formation in vitro [7] and reversed-phase liquid chromatography [8]. In such applications, the knowledge of solute molecular mobility in gels before and after volume phase transition is of great importance. Diffusion coefficient of a selected probe can also provide some information on the structure of the gel.

Experimental methods used to study molecular diffusion in gels include electrochemical [9,10] and radioactive tracer [11] techniques, and pulsed-field-gradient-spin-echo NMR [12]. Electrochemical methods provide a fast, inexpensive and accurate approach to such studies. They have been employed to study transport properties of NIPA-AA gels [9], polyacrylamide gel films [13], and polyelectrolyte solutions [14].

In this work, voltammetry and chronoamperometry were employed to investigate transport of electroactive probes in NIPA hydrogels. Steady-state voltammetry at microelectrodes was used in swollen gels; the concentration of the electroactive probes is well defined in those systems and can be

controlled during the preparation process. The following equation illustrates the relationship between the diffusion coefficient of electroactive species, D, and the steady-state current, I_s, at a microdisk electrode

$$D = I_s/4nFcr_d \qquad (1)$$

where n is number of electrons transferred, F is the Faraday constant, c is the concentration of an electroactive probe, and r_d is the radius of a microelectrode.

After the gel collapses as a result of the volume phase transition, the concentration of a probe in the polymeric phase may vary from that in swollen gel; the partition coefficient of electroactive probe between the NIPA polymer phase and the aqueous phase is not known. Chronoamperometry at microelectrodes was used to determine the diffusion coefficient of species in these cases where concentration was not known. The diffusion coefficient of the electroactive species can be determined from the slope of the linear dependence of I_t/I_s on $t^{-1/2}$, based on equation [15]

$$\frac{I_t}{I_s} = 1 + \left(\frac{2r_d}{\pi\sqrt{\pi Dt}}\right) \qquad (2)$$

where I_t is the current at the time t. This method was successfully used to determine the diffusion coefficient of electroactive probes encapsulated in a silicate gel prepared using the sol-gel process [16], and it allows one to obtain diffusion coefficients without knowing the exact concentration of the electroactive probe.

EXPERIMENT SECTION

Reagents. N-isopropylacrylamide (NIPA), N,N'-methylenebisacrylamide (BIS), N,N,N',N'-tetramethylethylenediamine (TMED), potassium iodide, ammonium persulfate and lithium perchlorate were purchased from Aldrich. 1,1'-Ferrocenedimethanol, $Fc(MeOH)_2$, was purchased from Fluka. All chemicals were used as received. All solutions were prepared using high purity water obtained from a Milli-Q (Millipore Model RG) purification system.

Apparatus. Voltammetric measurements were carried out in a jacketed glass cell with a three-electrode system consisting of an Ag/AgCl reference electrode or a Pt pseudo-reference electrode, a Pt wire counter electrode, and Pt microdisk working electrodes of a radius of 13.0 and 11.0 μm (Project Ltd., Warsaw, Poland). Working electrodes were polished with 0.1 μm diamond suspension using Microcloth polishing cloth (Buehler) before measurements. Optical inspection of the state of the electrode surface was accomplished with an inverted microscope for reflected light (Nikon, Model Epiphot-200). A refrigerated circulator (Isotemp model 1016P, Fisher Scientific) controlled the temperature of the cell. Staircase voltammetry and chronoamperometry were applied with a model 283 potentiostat (Perkin-Elmer, PARC) and controlled via a PC computer. Chronoamperometry experiments were conducted in a Faraday cage. The experimental parameters for chronoamperometry were: pulse time 20 s and sample frequency 50 Hz; 20 scans were collected for each temperature. The parameters for staircase voltammetry were: step height 3 mV and frequency 5 Hz. An average of current signals from at least 5 measurements was used to calculate the corresponding diffusion coefficient. UV/vis spectra were obtained using a Hitachi model U-2001 UV/vis spectrophotometer. The dry NIPA polymer was ground using a Bel-Art micro-mill.

Gel preparation. The synthesis of a NIPA copolymer cross-linked with BIS was modified from a previously reported procedure [17]. The polymeric gel was synthesized by conventional radical

polymerization; 0.87 g of NIPA and 0.0156 g of N,N'–methylenebisacrylamide (BIS) (cross-linker) were dissolved in 10 mL of distilled water. The pregel solution was placed in a water bath and deoxygenated with argon for 20 minutes. 5 mg of ammonium persulfate (initiator) was added to the solution followed by 56 μL of N,N,N',N' - tetramethyl-ethylenediamine (TEMED) (accelerator). The polymerization occurs at 22 °C and takes approximately 20 hours.

The freshly prepared gel was purified by a sponge-like method [9] to remove the unreacted compounds (monomers, initiator), and dried in an oven at 80 °C for two days. The dry polymer was ground by micro-mill before use. To prepare NIPA hydrogels with a well defined concentration of an electroactive probe, a known volume of a solution with an appropriate concentration of $Fc(MeOH)_2$ and supporting electrolyte, $LiClO_4$, and a known amount of dry NIPA polymer was left at room temperature for two, three days, to allow the polymer to swell and produce a gel.

analysis of diffusivity of $Fc(MeOH)_2$ in NIPA gels. The experimental activation energy of diffusion is 18.9, 18.5, and 18.6 kJ/mol, for 0.1 M $LiClO_4$ solution, 1.1% and 2.4% NIPA gels, respectively. The similar activation energy of diffusion in gels and in an aqueous solution shows that the local viscosity of a solution immobilized in NIPA gels is similar to that of the solute in an aqueous solution without the polymeric network.

The small decrease of the diffusion coefficient in polymeric gels compared to solutions without polymeric network can be explained by the "obstruction effect" and the "hydration effect" [20]. For dilute gels, the dependence of the diffusion coefficient of species on polymer concentration can be describe as [21]:

$$D'/D_0 = -1.667H\varphi + 1 \qquad (4)$$

where D' and D_0 are diffusion coefficients of species in gel and aqueous solution, respectively, φ is the weight fraction (concentration) of the polymer in the gel, H is hydration coefficient, which is related to the degree of hydration of the polymer. Figure 3 shows the dependence of the diffusion coefficient of $Fc(MeOH)_2$ on the concentration of NIPA polymer in the hydrogel. This dependence can be described by the linear equation $D'/D_0 = -5.54\varphi + 0.998$ with a correlation coefficient of 0.995. The H-parameter determined from our experiments is 3.22, which is much smaller than that determined previously for poly(*N*-isopropylacrylamide-*co*-acrylic acid) hydrogel, 8.77 [21]. This difference is easy to understand if one remembers that a polymer containing ionic groups like acrylate has a much larger degree of hydration than nonionic polymer.

The theory of the kinetics of spherical gel swelling and shrinking was proposed by Tanaka and Fillmore (the TF theory) [22]

$$\tau \approx R^2/D \tag{5}$$

where τ is the characteristic time for gel swelling or shrinking, R and D are the radius of the gel and the cooperative diffusion coefficient of the gel, respectively. Although the TF theory was originally proposed for spherical gels, several modifications to the model based on TF theory were successfully developed for cylinders and large disk gels [22,23]. The TF theory suggests that the time of the volume phase transition of gels depends on the size of gels, the smaller the gel the faster the gel can shrink or swell. Recent differential scanning calorimetry (DSC) studies have shown that small size NIPA gel (0.3 mm in diameter) undergoes the volume phase transition in several minutes. However, for large size NIPA gel (3 mm in diameter), volume decrease was very slow, and the volume phase transition could not occur during the DSC experiment [6]. To minimize uncertainties of the kinetics effect of volume phase transition in our experiments, dry NIPA crosslinked polymer was ground using a micro-mill. Very fine NIPA polymer powder was obtained. An inverted microscope was used to determine the size of the polymeric particles. The major fraction of these particles (approximately 90%) has a radius smaller than 0.1 mm. The NIPA hydrogel with small gel size was prepared using that ground polymer. After the swelling process, separation of a single swollen particle of the gel, and a measurement of the size of that particle was not possible. The NIPA gel prepared by this method undergoes a volume phase transition at a temperature of 32 ± 1 °C, and this transition results in a release of approximately 93% of the solvent from the polymeric phase. After the volume phase transition, the small-size NIPA gel particles did not separate; the polymer phase collapsed forming one large piece of a rubber-like polymeric phase.

Transport of $Fc(MeOH)_2$ in the collapsed NIPA gels was first studied using steady state voltammetry. We found that above the temperature of the volume phase transition, oxidation current of $Fc(MeOH)_2$ probe dropped significantly. Figure 4 compares two voltammograms of the oxidation of 2

mM $Fc(MeOH)_2$ in 3 % NIPA gel at 27.5 and 40 °C, and Figure 5 shows the dependence of the limiting current on the temperature, from 20 to 65 °C. As one can see after the volume phase transition, the steady state current drops almost to zero, which suggests that the diffusion coefficient decreases significantly. However, the observed decrease of the limiting current in collapsed gels might also be due to the change of the concentration of $Fc(MeOH)_2$ in the collapsed phase, see eq. 1. At the same time the reproducibility of the limiting current is much worse than that for swollen gels. The relative standard deviation, *rsd*, of limiting currents after the phase transition is 42%, while for swollen gels *rsd* is less than 5%. This can be due to the inhomogeneous distribution of an electroactive probe in the collapsed polymeric phase or due to inhomogeneity of the collapsed polymeric phase.

Since the concentration of the probe in the collapsed gel is not known, chronoamperometry was applied to measure the diffusion coefficient of electroactive probes in collapsed gels. According to eq. 2, the plot of an average current as a function of $1/t^{1/2}$ should be linear with a slope $S = \frac{2r_d}{\pi\sqrt{\pi D}}$. Therefore, the diffusion coefficient of probes can be calculated using the following dependence:

$$D = \left(\frac{2r_d}{S\pi\sqrt{\pi}}\right)^2 \qquad (6)$$

Figure 6 shows the transient current, I_t, as a function of $t^{-1/2}$. Linear dependence was obtained as predicted by eq. 2. Diffusion coefficients of $Fc(MeOH)_2$ in 3% NIPA collapsed gels were calculated based on eq. 4, and are 1.6×10^{-8}, 2.8×10^{-8}, and 4.5×10^{-8} cm^2/s for 40, 50 and 60 °C, respectively.

As one can see, the diffusion coefficient of $Fc(MeOH)_2$ in collapsed gels is approximately two orders of magnitude smaller than that in 3% NIPA swollen gels, 5.4×10^{-6} cm^2/s at 25 °C. Due to a loss of 93% of the solvent during the volume phase transition, the polymer phase is very dense and

the liquid channels for molecular/solvent transport are considerably restricted, resulting in a decrease of the diffusion coefficient of the probe in the collapsed phase.

Since $Fc(MeOH)_2$ aqueous solution has an absorption band in the UV-vis range with a maximum absorbance at 430 nm [9], UV-vis spectroscopy can be used to study the distribution of $Fc(MeOH)_2$ between the collapsed polymer phase and released solution, and determine changes of its concentration as a result of the volume phase transition. The concentration calibration plot was prepared using standard $Fc(MeOH)_2$ aqueous solutions with the concentration range from 1 to 6 mM. Three NIPA hydrogels with various polymer concentrations were prepared. Each gel contained 2 mM $Fc(MeOH)_2$. After the gel collapsed, the solution expelled from the gel was collected. The absorbance of that solution was measured and the concentration of $Fc(MeOH)_2$ was determined based on the concentration calibration plot. Table 1 presents concentration of $Fc(MeOH)_2$ in expelled solutions for several compositions of NIPA gels. As one can see the concentration of $Fc(MeOH)_2$ in the released solution is lower than that in the original swollen gel. Since the total volume of released liquid and collapsed gel is identical to that of swollen gel, this means that the concentration of $Fc(MeOH)_2$ in the collapsed gel is higher than that in swollen gel. This indicates strong interactions between $Fc(MeOH)_2$ and the NIPA polymeric network. These might be due to hydrophobic interactions and/or van der Waals interactions. For the 3% NIPA gel with 2 mM $Fc(MeOH)_2$ in the swollen state, we found that after passing through the volume phase transition the concentration of the probe in the released solution is 1.5 mM. Based on the volume of the released solution, the number of moles of $Fc(MeOH)_2$ in the swollen gel, and the mass of the collapsed gel, with the assumption of that density of polymeric phase is close to that of aqueous solution, we can estimate the concentration of $Fc(MeOH)_2$ in the collapsed gel as 9 mM, 4.5 times higher than that in the original swollen gel and 6 times higher than that in released liquid.

Now we can compare transport results obtained by two electroanalytical methods, voltammetry and chronoamperometry. Steady state voltammetric currents in the collapsed polymer phase for 3% NIPA gel were 0.089 nA and 0.17 nA for 50 and 60 °C, respectively. The corresponding diffusion coefficients calculated from those currents and concentration of $Fc(MeOH)_2$ determined from UV/vis experiments, 9 mM, are $2.4\times10^{-8}cm^2/s$ and 4.5×10^{-8} cm^2/s for 50 and 60 °C, respectively. Comparison of those values with diffusion coefficients determined from concentration independent normalized chronoamperometry (2.8×10^{-8} and 4.5×10^{-8} cm^2/s for 50 and 60 °C, respectively) shows that they are the same within experimental error.

Summary

Two electroanalytical methods, steady state voltammetry and chronoamperometry at platinum microelectrodes, were used to determine the diffusion coefficient of $Fc(MeOH)_2$ in swollen and collapsed NIPA hydrogels. The mass transport properties of swollen gels are similar to those of aqueous solutions free of polymeric network. The volume phase transition of NIPA gels occurs at 32 °C, and results in a release of approximately 93% of the solution from the polymeric network. After the phase transition, the diffusion coefficient of $Fc(MeOH)_2$ in the collapsed gel phase decreases by two orders of magnitude. Additionally, the concentration of $Fc(MeOH)_2$ in a gel phase changes as a result of volume phase transition, and as shown by UV/vis spectroscopic results for 3% NIPA gel it is 4.5 times higher in the collapsed phase than that in the swollen gel.

Comparison of transport properties of NIPA and NIPA-AA hydrogels [21] in their swollen state shows that the "hydration effect" (interactions between polymeric network and water) is much stronger for ionic NIPA-AA gels than for NIPA gels. The diffusion coefficient of $Fc(MeOH)_2$ in 3 % NIPA gel at 25 °C is 5.4×10^{-6} cm^2/s, while in 3 % NIPA-AA (mole ratio of NIPA to AA 95:5), at the

same temperature, it is 3.4×10^{-6} cm^2/s, compared to 6.4×10^{-6} cm^2/s in a solution without polymeric network. However, for collapsed gels after the volume phase transition, transport properties of NIPA and NIPA-AA gels are extremely different. For NIPA collapsed gels diffusion coefficient of $Fc(MeOH)_2$ is two orders of magnitude lower that that in swollen state or solution, while for NIPA-AA hydrogels, the mass transport does not change significantly as a result of that transition [24]. This is probably due to changes of the free volume in collapsed gels; NIPA gels change volume by as large as 93%, while for NIPA-AA gels that change is approximately 40%.

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Table 1. Concentration of $Fc(MeOH)_2$ in swollen gels and expelled solutions.

	Concentration of $Fc(MeOH)_2$ / mM	
NIPA (w/w) %	Swollen Gel	Expelled Solution
1.7%	2.0	1.7
2.6%	2.0	1.6
3.0%	2.0	1.5

FIGURE CAPTIONS

Figure 1. Steady-state voltammogram of the oxidation of (**A**) 2 mM $Fc(MeOH)_2$ in 3% (w/w) NIPA gel, (**B**) background; 0.1 M $LiClO_4$, Pt microdisk electrode, r_d = 11 μm, 25 °C.

Figure 2. Arrhenius plots for the temperature dependence of the diffusion coefficient of $Fc(MeOH)_2$ in NIPA hydrogels: ♦ 1.7%, ■2.4%, •3.0% (w/w) of polymer in the gel.

Figure 3. Dependence of the diffusion coefficient of $Fc(MeOH)_2$ in NIPA hydrogel on the concentration of the polymer in the gel; best fit $D'/D_0 = -5.54\varphi + 0.998$, φ is the weight fraction of the polymer in the gel.

Figure 4. Voltammograms of oxidation of 2 mM $Fc(MeOH)_2$ in 3% (w/w) NIPA gel before and after volume phase transition at 27.5 and 40 °C; 0.1 M $LiClO_4$, Pt microdisk electrode, r_d=11 μm.

Figure 5. Steady state current of oxidation of 2 mM $Fc(MeOH)_2$ in 3% (w/w) NIPA gel for the temperature range 20 – 65 °C; 0.1 M $LiClO_4$, Pt microdisk electrode, r_d=11 μm.

Figure 6. Plot of the experimental I_t/I_s *vs.* $t^{-1/2}$ for the oxidation of $Fc(MeOH)_2$ in 3% NIPA gel at a r_d=11 μm Pt electrode at 40 °C; the transient current is also shown.

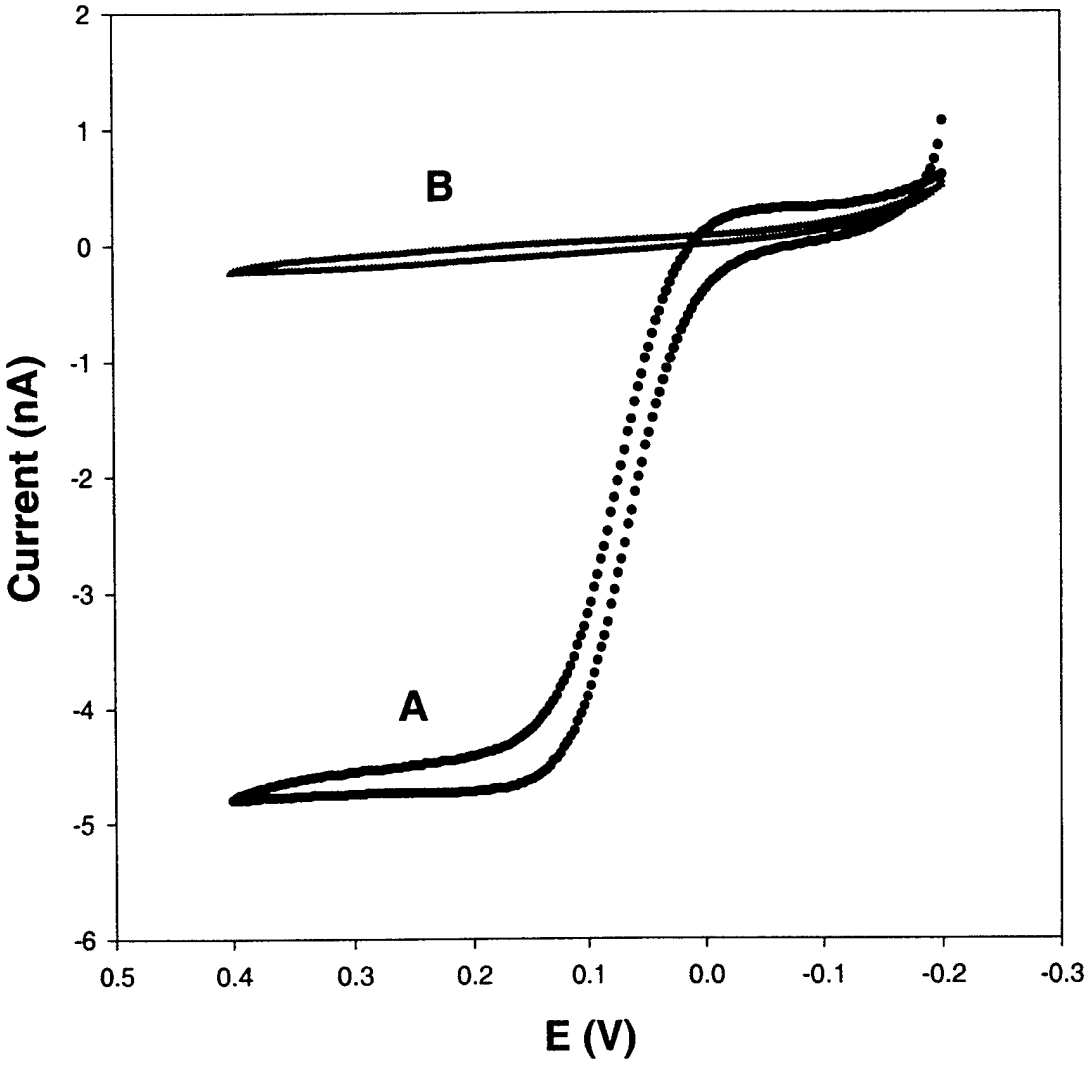
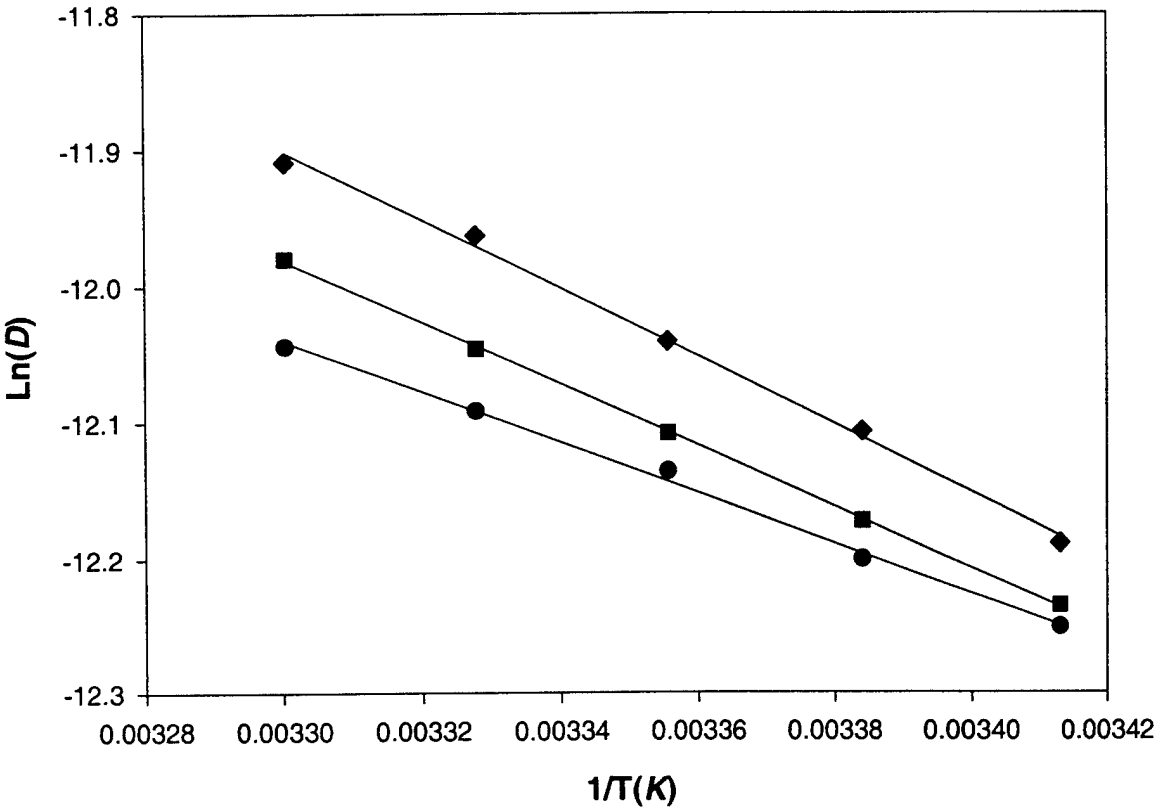


Figure 1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-12.1
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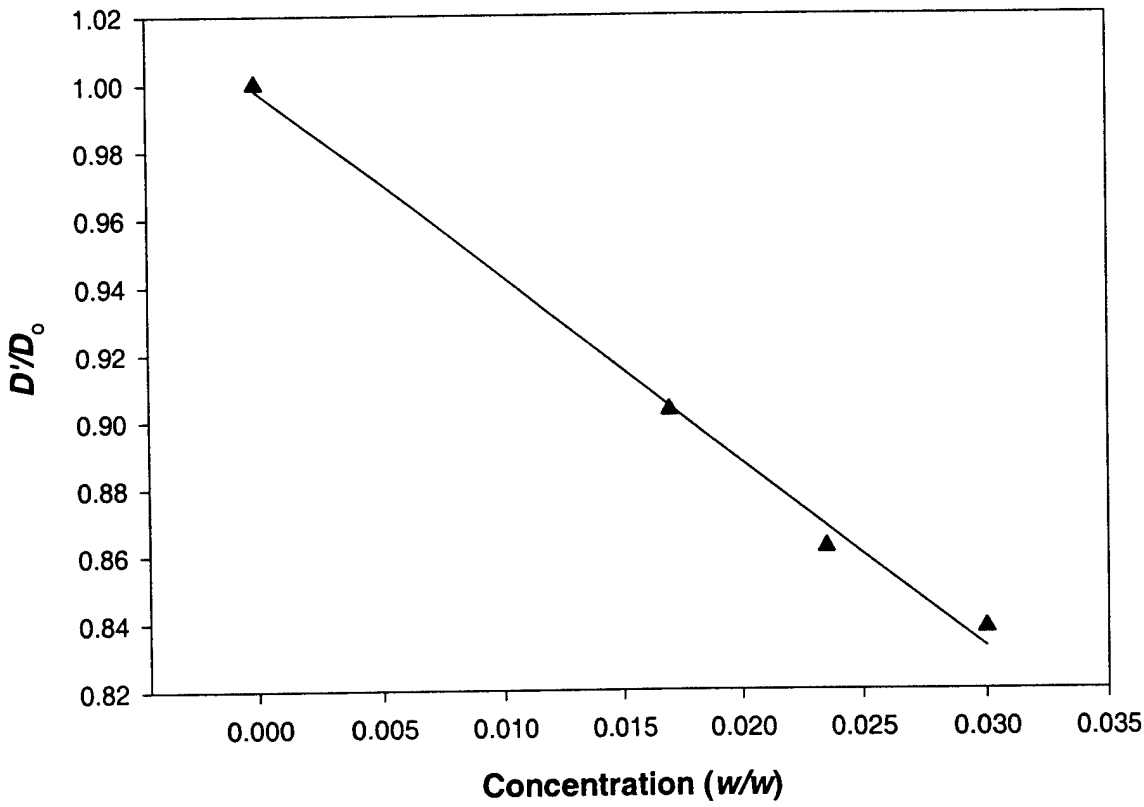
1/T(K)

Figure 2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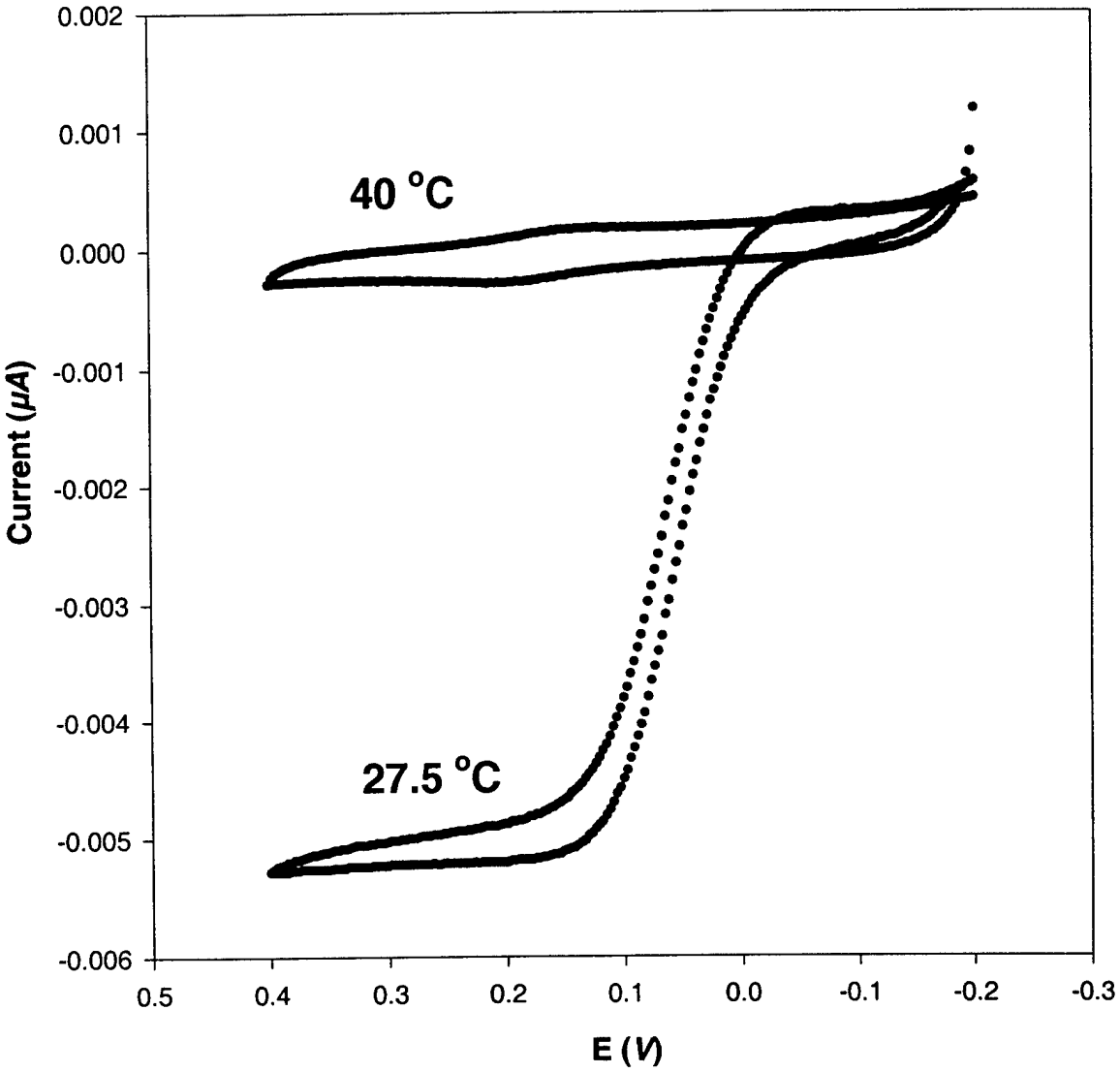
Concentration (w/w)

Figure 3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-0.2
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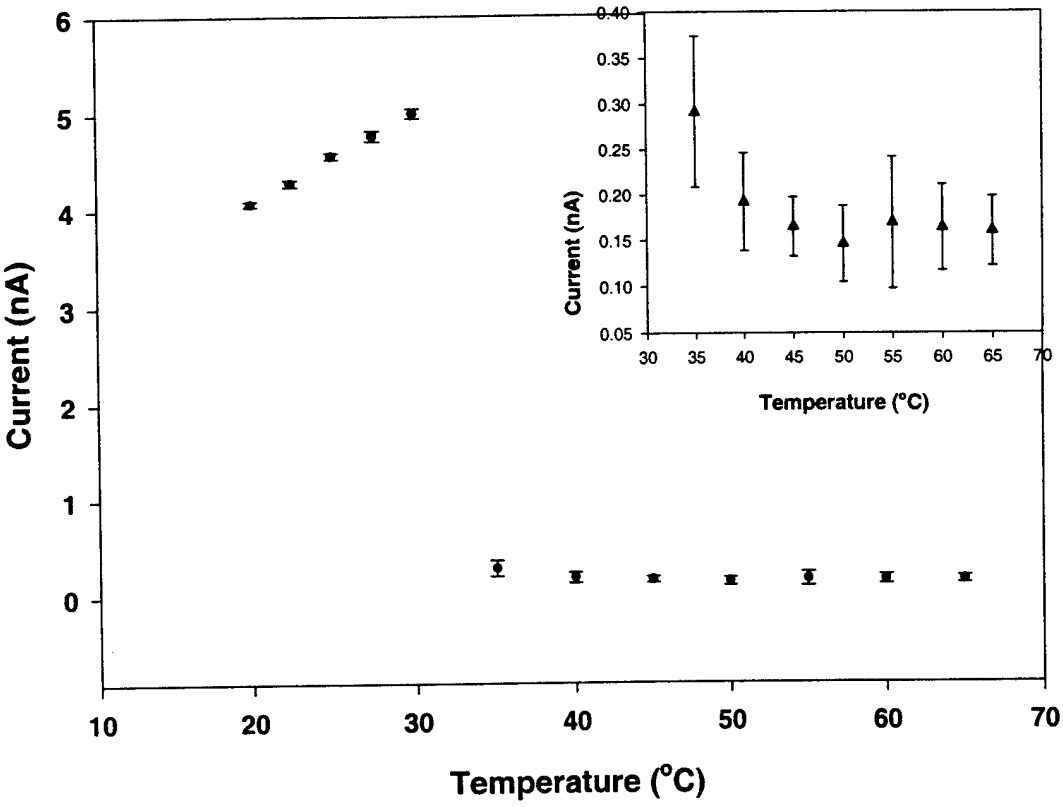
E (V)

Figure 4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Temperature (°C)
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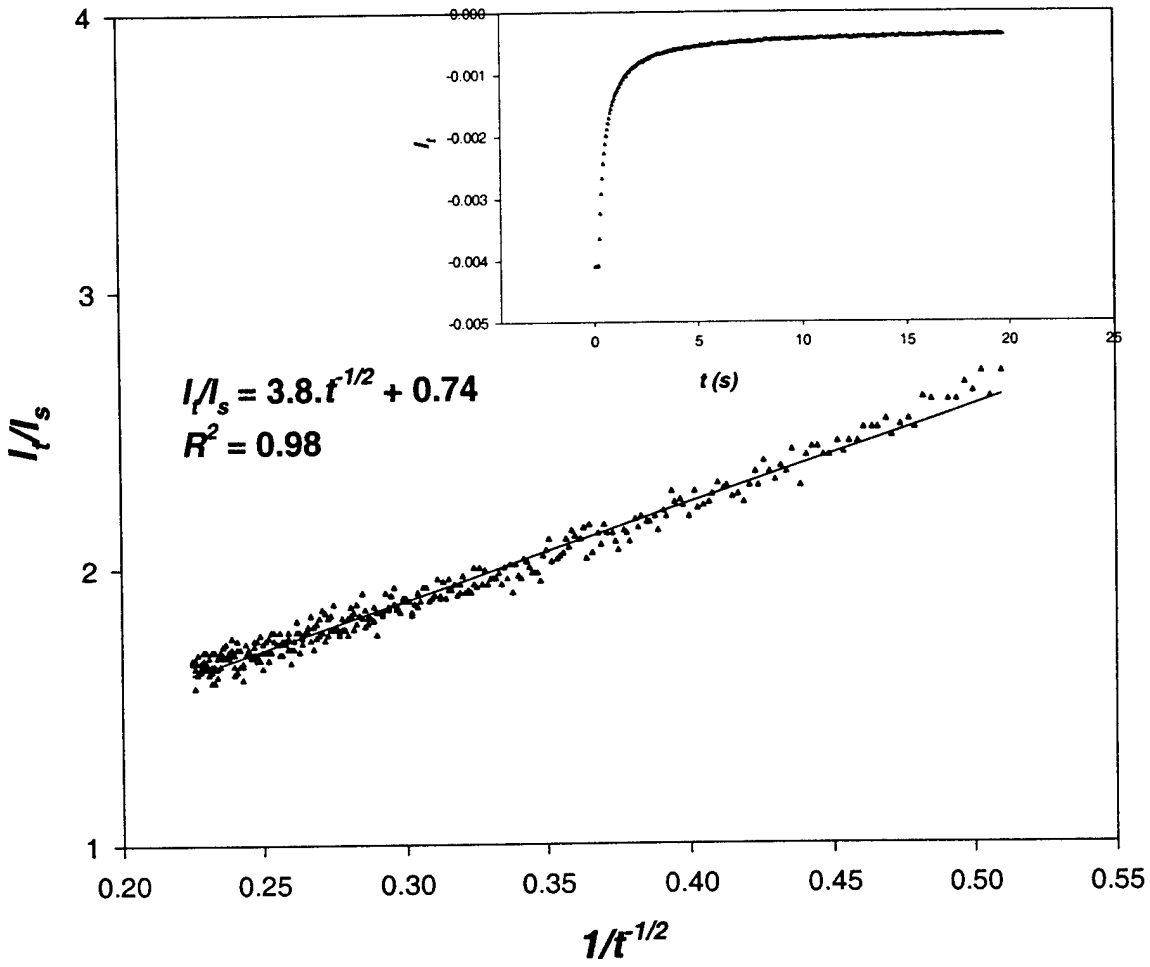
Figure 5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0.45
0.50
0.55
I_t/I_s
$1/t^{1/2}$
$I_t/I_s = 3.8.t^{-1/2} + 0.74$
$R^2 = 0.98$
0.000
-0.001
-0.002
-0.003
-0.004
-0.005
I_t
0
5
10
15
20
25
t (s)

Figure 6