Effect of the Volume Phase Transition on Diffusion and Concentration of Molecular Species in Temperature-Responsive Gels: Electroanalytical Studies

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Effect of the volume phase transition on the diffusion and concentration of molecular probes was studied in temperature-responsive polymeric hydrogels. Results were compared for two gels, poly(*N*-isopropylacrylamide), NIPA, and poly(*N*-isopropylacrylamide-*co*-acrylic acid), NIPA-AA. These gels undergo discontinuous, reversible volume phase transition as a response to temperature changes; this transition results in release of approximately 40% and 90% of the solution/solvent from NIPA-AA and NIPA gel phases, respectively. 1,1'–ferrocenedimethanol, $Fc(MeOH)_2$, served as an electroactive and spectroscopic probe. Diffusion of $Fc(MeOH)_2$ was investigated using voltammetry and chronoamperometry with platinum disk electrodes, while UV-vis supported electroanalytical techniques to determine the concentration of that probe in the gel. The diffusion coefficient of $Fc(MeOH)_2$ was inversely proportional to the concentration of the polymer in both NIPA and NIPA-AA swollen gels for temperatures below the volume phase transition (swollen gels), and differed from that in an aqueous solution (see Figure 1 and Table 1). The diffusion coefficient was 16 and 46% smaller than that in an aqueous solution for 3% NIPA and NIPA-AA gels at 25 °C, respectively. Identical activation energy, E_a, of diffusion in both gels and aqueous solution suggests that the microscopic viscosity in a gel is similar to that of an aqueous solution, even if the macroscopic viscosity is very large.

Table 1. Diffusion coefficient, D, and activation energy of diffusion, E_a, of $Fc(MeOH)_2$ in various media, and macroscopic viscosity, η, of those media; 0.1 M $LiClO_4$.

Medium	D / cm^2/s @ 25 °C	E_a / kJ/mol	η / cP
Aqueous solution	$6.4 \times 10^{-6} \pm 3.9 \times 10^{-7}$	18.9 ± 0.23	9.4×10^{-1}
2.4 %NIPA gel	$5.5 \times 10^{-6} \pm 1.7 \times 10^{-7}$	18.6 ± 0.29	1.5×10^{5}
2.0 % NIPA-AA gel	$4.4 \times 10^{-6} \pm 5.6 \times 10^{-8}$	19.2 ± 0.18	2.0×10^{5}

As a result of the volume phase transition, after the gel collapses, no significant changes in the diffusion coefficient values were observed for NIPA-AA gels. However, for NIPA gels, the diffusion coefficient of a probe decreases approximately two orders of magnitude (see Figure 2). This striking difference can be attributed to a different swelling ratio of both polymeric gels in their collapsed state. For NIPA gels that release approximately 90% of a solvent as a result of the volume phase transition, liquid channels in a collapsed phase are considerably restricted for molecular/solvent transport. Relatively open structure exists in collapsed NIPA-AA gels, and therefore, transport of species is not influenced significantly by the volume phase transition.

The volume phase transition also resulted in a change of the concentration of a probe in the collapsed gel phase (see Table 2). The concentration of $Fc(MeOH)_2$ in collapsed NIPA gel was as much as 4.5 times higher than that in the original swollen gel, while for NIPA-AA gel that increase in concentration was only 20%.

Table 2. Concentration of $Fc(MeOH)_2$ in 3% swollen gels, collapsed gels and expelled solutions.

Medium	D / cm^2/s @ 25 °C	E_a / kJ/mol	η / cP
Aqueous solution	$6.4 \times 10^{-6} \pm 3.9 \times 10^{-7}$	18.9 ± 0.23	9.4×10^{-1}
2.4 %NIPA gel	$5.5 \times 10^{-6} \pm 1.7 \times 10^{-7}$	18.6 ± 0.29	1.5×10^{5}
2.0 % NIPA-AA gel	$4.4 \times 10^{-6} \pm 5.6 \times 10^{-8}$	19.2 ± 0.18	2.0×10^{5}

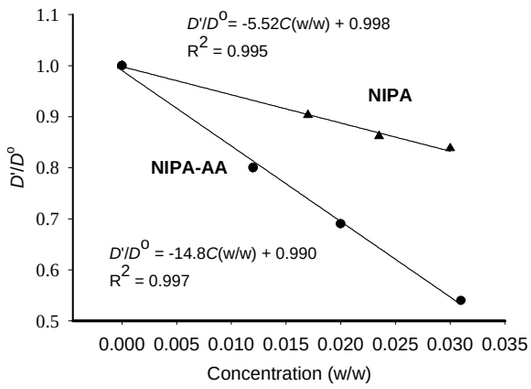

Figure 1. Dependence of the normalized diffusion coefficient, D'/D^0, of $Fc(MeOH)_2$ on the concentration of the polymer in a swollen gel; 25 °C, 0.1 M $LiClO_4$.

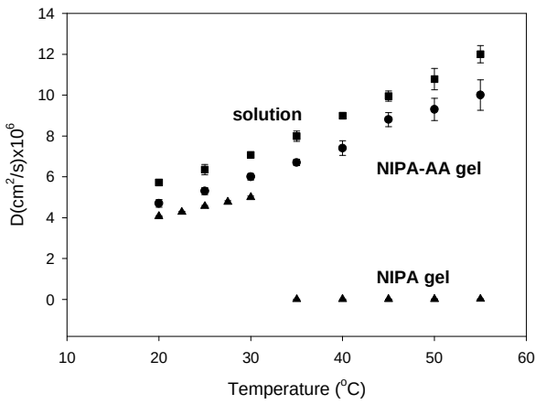

Figure 2. Diffusion coefficient of 1,1'-ferrocenedimethanol, $Fc(MeOH)_2$, as a function of temperature; 0.1 M $LiClO_4$ in all samples.