Mass Transport in Swollen Thermoresponsive Hydrogels: Theoretical Model and Electroanalytical Studies

Malgorzata Ciszkowska and Weimin Zhang
Department of Chemistry, Brooklyn College, CUNY
Brooklyn, NY 11210-2889

Voltammetry and chronoamperometry at microelectrodes were used to study mass transport properties of temperature responsive poly(N-isopropylacrylamide-*co*-acrylic acid), NIPA-AA, hydrogels. These gels can discontinuously shrink or swell as a response to a change of temperature, with volume changes of approximately 40%. The volume phase transition temperature of NIPA-AA hydrogels varies from 33 – 40 deg C, and depends on the ratio of the two monomers and the ionic strength of the solvent/solution.

1,1'-Ferrocenedimethylanol, $Fc(MeOH)_2$, and 2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO, were used as electroactive probe molecules. The activation energy of diffusion of $Fc(MeOH)_2$ in aqueous solutions and in NIPA-AA hydrogels was found to be in the range of 17 - 19 kJ/mol, which suggests that the local microscopic viscosity does not change significantly due to the gelation process, although the macroscopic viscosity of the gels is extremely large.

It was found that the diffusion coefficients of $Fc(MeOH)_2$ and TEMPO in NIPA-AA hydrogels in their swollen state are approximately 20% - 50% smaller than those in aqueous solutions, and that the diffusion coefficient of probe molecules in these gels is inversely proportional to the concentration of co-polymer in the hydrogels. and the "obstruction effect" and "hydration effect" were used to explain this phenomenon.

A new theoretical model was developed and a modified equation taking into account the "obstruction effect" and "hydration effect" was proposed. Experimental results were compared with predictions of the model, and the diffusion coefficient of TEMPO in the NIPA-AA gel was successfully predicated based on that new model (see Figure 1).

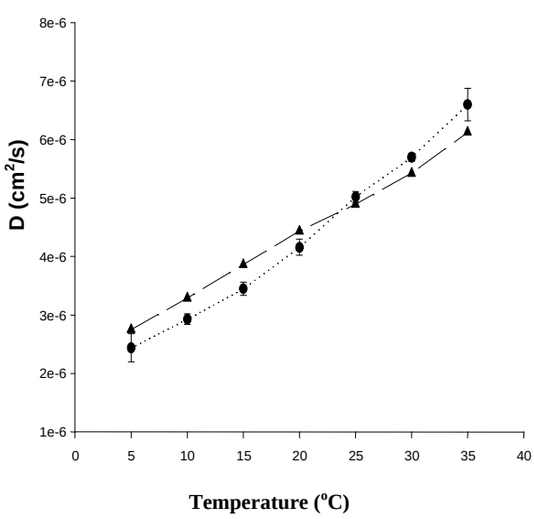

Figure 1 Temperature dependence of the diffusion coefficient of TEMPO in 2.0 % (w/w) NIPA-AA gel; (▲) calculated values, (●) experimental values.