

Comparison of the Mobility of Small Molecules in Molecular and Polymer Hydrogels

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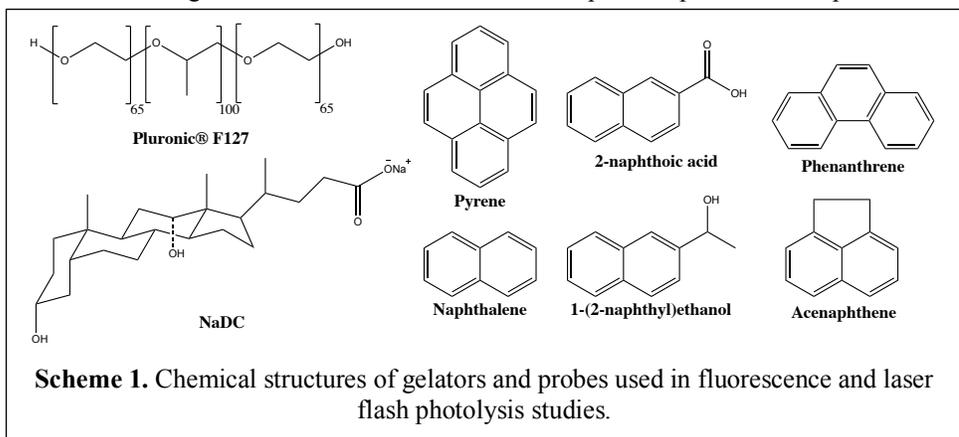
Research Progress Report: The ACS Petroleum Research Fund award has supported a new direction in my research group where we investigate the mobility of small molecules through two different types of hydrogel systems (Scheme 1) over different length scales. The overall objective is to determine the degree of control that can be achieved for the mobility of small molecules in a molecular gel compared to a polymer gel. Pluronic® F127 is a polyethyleneoxide-polypropyleneoxide-polyethyleneoxide (PEO-PPO-PEO) triblock copolymer that forms polymer gels above a certain gelator concentration and when the temperature is raised. The gel is formed through the dehydration of the PPO micelle cores. Sodium deoxycholate (NaDC) forms a low molecular weight supramolecular gel at certain pH ranges when gelation of the NaDC aggregates in the sol occurs. Photophysical methods including steady-state and time-resolved fluorescence quenching, laser flash photolysis and absorption studies were employed to determine the movement of small molecules through NaDC and F127 gels. The first phase of the project was to develop methodology for these studies, based on methodology previously used in solution (Post-doc – S.S. Thomas).

Small molecules of different hydrophobicities distribute themselves differently in the various regions of the gel. Quenching studies of excited-states are used to measure the mobility of the quencher or of the probe in its excited state. If the lifetime of the excited state of the probe is short then the probe cannot move over a long distance while in its excited state. In this case, the probe is seen as stationary and the mobility of the quencher is measured. The quenching rate constants are a measure of the accessibility of the quencher to the environment in which the probe resides. Steady-state and time-resolved fluorescence studies were performed with gel samples. Scattering from the gel constitutes an experimental challenge when the usual 90° geometry between the excitation beam and collection optics for the emission is used. In the case of F127, the scattering from the gel was minimal and the usual 90° geometry can be used. In the case of NaDC gels, scattering from the sample is significant. For experiments at room temperature a front-face arrangement could be used, where the excitation beam and the emission are collected from one side of the cell. However, for studies at different temperatures the usual 90° geometry had to be used and new analysis methods were developed that considered the scattering from the sample.

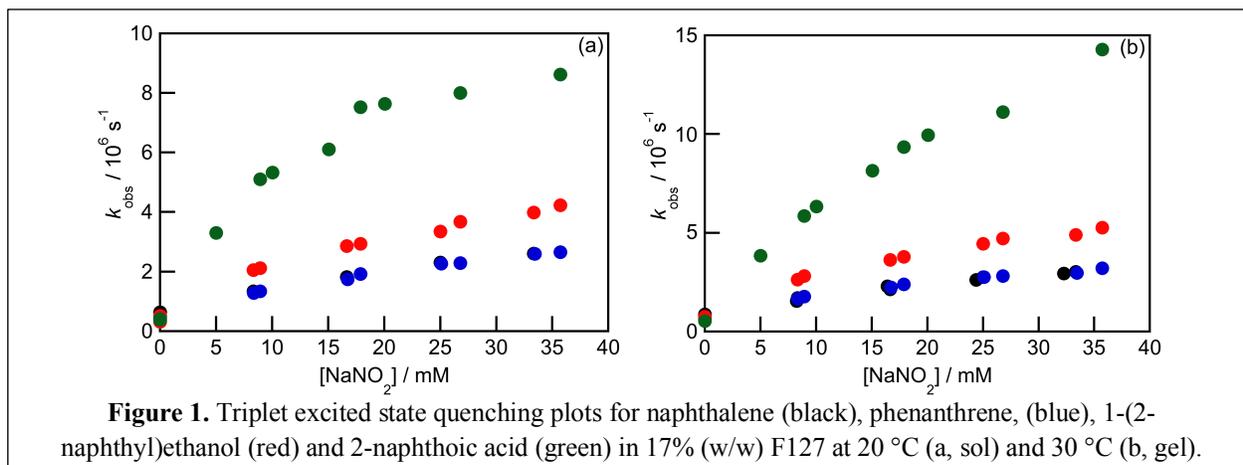
Lifetimes of triplet excited state of probes are sufficiently long that the triplet excited state probe can move between the different environments of the gel during its excited state lifetime. The dependence of the observed rate constants with quencher concentrations deviates from the linear dependence seen in homogeneous solution. This deviation is a consequence of the different quenching efficiencies for the different environments and the association and dissociation rate constants of the probes with the various environments in the gel. These studies provide information on the mobility of probe and quencher over nm to μm.

Mobility of small molecules over the cm length scale were studied with a custom-built system where samples are irradiated at the bottom or the top of the cell and the absorption or fluorescence of the sample is measured at a distance from the irradiation area. The system consists of two irradiation lamps, one for the irradiation at the top or bottom of the cell and the other lamp for the monitoring of molecules in the center of the sample. Samples can be kept at constant temperatures making it possible to study materials in the gel and sol phases.

In the case of F127, the PPO core is more hydrophobic compared to the PEO corona and the surrounding water molecules. Quenching of the singlet excited states of pyrene and naphthalene with two quenchers of different

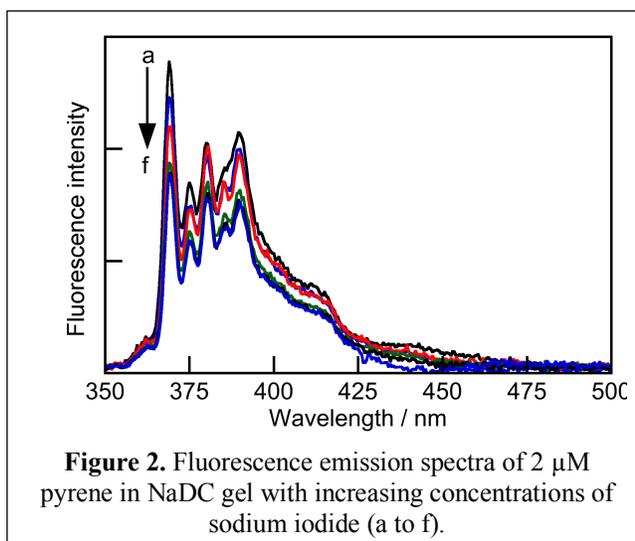


hydrophobicities (sodium iodide and nitromethane) gave us information about the diffusion rate of the quenchers on the nanometer length scale, where the quencher reacted with the shorter-lived singlet excited state of pyrene molecules located in the more hydrophobic regions of the gel. The quenching with sodium nitrite of the longer-lived triplet excited state of small probe molecules of different hydrophobicities (see polyaromatic hydrocarbons in Scheme 1 with exception of pyrene and acenaphthene) through laser flash photolysis studies allowed us to determine the association and dissociation rate constants for the movement of these probes between different environments in F127 gel and sol systems (Figure 1). The association and dissociation kinetics of the probe molecules in F127 micelles was found to follow a trend dependent on the hydrophobicity of the probe (S.S. Thomas and MSc student H. Hosseini Nejad).



In another approach, we developed a method in which the diffusion kinetics of a photochromic diarylethene compound (DAE) in F127 over the cm length scale was monitored by absorption measurements. The thermodynamically stable and colorless open form of DAE isomerises into the colored closed form upon photo irradiation by UV light. In our experiments the absorption from a non-irradiated part of the gel was measured over time, which was located 1-2 cm apart from the area in the gel that was irradiated with UV light. This method is used to map the movement of the DAE molecules from one part of the gel to the other on a macroscopic length scale. The dependence of the diffusion kinetics on the gelator's concentration and temperature is being investigated (S.S. Thomas). Currently systematic studies are being performed in which the concentration of F127 and temperature are being varied to determine if the mobility of small molecules is affected by changes to the structure of the gel.

Fluorescence quenching of probes of different hydrophobicities in NaDC gels (Figure 2) yielded evidence of three different microheterogeneous environments in which these probes localize. Probe molecules located in the most protected hydrophobic regions of the gel are quenched less efficiently compared to probes located in less hydrophobic environments. The quenching rate constants obtained from the analysis of the experimental data gave information on the mobility of the quenchers in different environments in the gel (PhD student A. Awasthi). Currently the effect of systematic changes in concentration are being investigated.



Impact on the Research Team's Career: Post-doc Thomas was given the opportunity to develop all the methodology for the proposal, which was the biggest challenge since these types of measurements with gels had not been performed previously. She is currently seeking employment in industry. Her track-record of working independently and of supervising students has been valuable for her employment prospects. MSc student Hosseini Nejad has presented her results at the PoND CREATE training program research day and at the 102nd CCCE. PhD student A. Awasthi presented his results at the PoND CREATE research day.