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Fluorescence Techniques

CMC Determination using Fluorescence Probes. CMC values of SDS and Tween 80 were determined by monitoring changes in the fluorescence intensity of naphthalene and phenanthrene, respectively, as a function of surfactant concentration. Three milliliters of a fluorescence probe solution (0.1 M NaCl) was pipetted into a fluorescence cuvette and then mixed for approximately 30 min with a Teflon-covered micro stir bar to pre-equilibrate the cuvette and stir bar. Nominal concentrations for phenanthrene and naphthalene were 2.24 and 78 μM , respectively. When the absorbance and fluorescence intensity stabilized, the values were recorded and the sample then titrated with a series of 10 μL aliquots of surfactant stock solution. Because the volume of the spiked surfactant solutions was small, dilution effects were negligible.

As shown in Figure 1, surfactant titrations of solutions containing fluorescent HOCs can give relatively well-defined predictions for their CMC values. When the surfactant concentration reaches the CMC, the fluorescence changes abruptly because of the change in the HOC microenvironment. From Figure 1, the CMC for SDS in 0.1 M NaCl was determined by a nonlinear fitting of the two distinct naphthalene fluorescence regions. The value obtained, 1.35 mM, agrees well with the results of previous studies for similar ionic strength conditions (19, 24, 32). The fluorescence change for phenanthrene in the presence of Tween 80 was not as dramatic as for naphthalene in SDS. Nevertheless, the CMC of Tween 80 as determined by linear regression of the two distinct fluorescence regions (9.16 μM or approximately 12 mg/L) is close to the value reported by Pennell et al. (10).

Micellar Solubilization of Fluorescence Probes. For determining K_{mic} values, batch experiments were conducted in triplicate using glass vials sealed with lead foil faced Teflon-lined caps. HOC concentrations were varied by spiking different amounts of individual stock solutions into 25 mL of 0.1 M NaCl solutions; any adverse co-solvent effects were minimal for

the low methanol volume fractions used (0.04% to 0.1% depending on HOC concentration). Surfactant stock solutions were then spiked into the HOC solutions such that the surfactant concentrations ranged from zero to well above the CMC. The samples were placed on a shaker for 3 days to equilibrate before spectroscopic analyses were conducted; this time period was chosen based on solubilization rate studies (see below). The absorbance and fluorescence intensity of each sample were measured and the results were analyzed to determine K_{mic} values. Blank tests with surfactants showed a negligible contribution to the background fluorescence; therefore, no corrections were necessary.

Addition of surfactant above the CMC results in the formation of micelles and the corresponding HOC solubilization into the hydrophobic region of a micelle, thereby increasing the apparent HOC solubility. A micellar partition coefficient, K_{mic} , representing the distribution of an HOC between the micellar pseudophase and the aqueous phase can be expressed by (33):

$$K_{mic} = \frac{C_{mic}}{C_w \cdot S_{mic}} \quad (1)$$

where C_{mic} and C_w are the HOC concentrations (μM) in the micellar and aqueous phases, respectively. S_{mic} is the concentration (mM) of surfactant molecules present as micellar species; for total surfactant concentrations above the CMC it is given by:

$$S_{mic} = (S_{surf} - \text{CMC}) \quad (2)$$

where S_{surf} is the total aqueous surfactant concentration. For a fluorescent HOC, the total fluorescence intensity per unit total HOC concentration (F_t) in a micellar solution is (18):

$$F_t = F_w \cdot \frac{C_w}{C_t} + F_{mic} \cdot \frac{C_{mic}}{C_t} \quad (3)$$

where C_t is the total HOC concentration present and F_w and F_{mic} are the fluorescence intensities

per unit HOC concentration in the aqueous and micellar phases, respectively. A mass balance on HOC gives:

$$C_t = C_w (1 + K_{mic} \cdot S_{mic}). \quad (4)$$

Combining eqs 1 through 4 gives a nonlinear equation relating total unit fluorescence to the surfactant concentration for systems at or above the CMC:

$$F_t = \frac{F_w + F_{mic} \cdot K_{mic} \cdot (S_{surf} - CMC)}{1 + K_{mic} \cdot (S_{surf} - CMC)} \quad (5)$$

Equation 5 shows that for a fixed total HOC concentration, $F_t = F_w$ when no micelles are present (i.e., $S_{surf} < CMC$) and that as $S_{mic} = (S_{surf} - CMC) \Rightarrow \infty$ F_t asymptotically approaches F_{mic} .

K_{mic} can be obtained from the curve as the value of $S_{mic}^{-1} = (S_{surf} - CMC)^{-1}$ at the point where $F_t = (F_w + F_{mic})/2$. For this work, however, K_{mic} , F_{mic} and F_w were determined by fitting eq 5 to the total fluorescence with a nonlinear least-squares curve fitting program (STATISTICA 4.0 for Windows, StatSoft, Inc.).

Preliminary Rate Studies

Preliminary rate studies were performed to determine the time periods necessary to reach an apparent equilibrium for surfactant sorption to kaolinite and HOC partitioning to micelles and the sorbed surfactants. In all cases, the above processes were observed to follow pseudo first-order rates and thus were subsequently modeled as such in the accompanying paper (34).

Representative rate data and model fits for HOC solubilization by SDS and Tween 80 micelles are shown in Figure 2. At about 48 hours, the fluorescence intensity of phenanthrene in both micellar solutions becomes constant with time, indicating equilibrium has been reached. Dulfer et al. (35) studied PCB partitioning in SDS solutions and obtained similar solubilization rates. Using fluorescence techniques to measure quencher diffusion rates into micelles, Gratzel and Thomas (36) concluded that a time period of about 40 hours was necessary for micelles to

become stable.

Representative results for surfactant sorption onto kaolinite are shown in Figure 3. Two SDS concentrations from different sorption regions were used to investigate potential differences in sorption rates. It is apparent that equilibrium is achieved within two hours and that similar sorption rates are obtained for the different SDS adsorption regions, indicating that whatever different sorption mechanisms are operative (e.g., sorbent-sorbate versus sorbate-sorbate interactions) in the two regions appear to have little effect on overall sorption rates. These observations are in general agreement with previous studies showing the rate of surfactant adsorption/desorption on soils to be rapid and essentially reversible (5, 37).

Phenanthrene partitioning to sorbed SDS is shown in Figure 4; the observed equilibration time of about 48 hours is close to that obtained for micellar partitioning (Fig. 2). However, it is clear in Figure 4 that normalized phenanthrene concentrations decrease very rapidly from 1.0 to about 0.05 and then decrease much more slowly to 0.03, indicating that partitioning to sorbed surfactant proceeds at a faster rate than it does to micelles. It is not clear whether this difference between micelles and sorbed surfactant is due to structural differences or aggregation densities; obviously a more detailed study is needed to elucidate these observations and to determine whether they are truly general results.

List of Figures (Supporting Information)

- Figure 1. CMC determination for SDS and Tween 80 by fluorescence of naphthalene and phenanthrene, respectively. Error bars for all data points are smaller than the symbols.
- Figure 2. Micellar solubilization of phenanthrene by SDS and Tween 80 at pH = 5.6 and ionic strength = 0.1 M NaCl. The solid line shows the fitting for the first-order solubilization rate by SDS and the dashed line shows the fitting for Tween 80
- Figure 3. SDS sorption on kaolinite at pH = 4.6 and ionic strength = 0.1 M NaCl. The lines show the fitting for the first-order sorption rates.
- Figure 4. Phenanthrene partitioning to sorbed SDS at pH = 4.6 and ionic strength = 0.1 M NaCl. The solid line shows the fitting for the first-order partitioning rate.

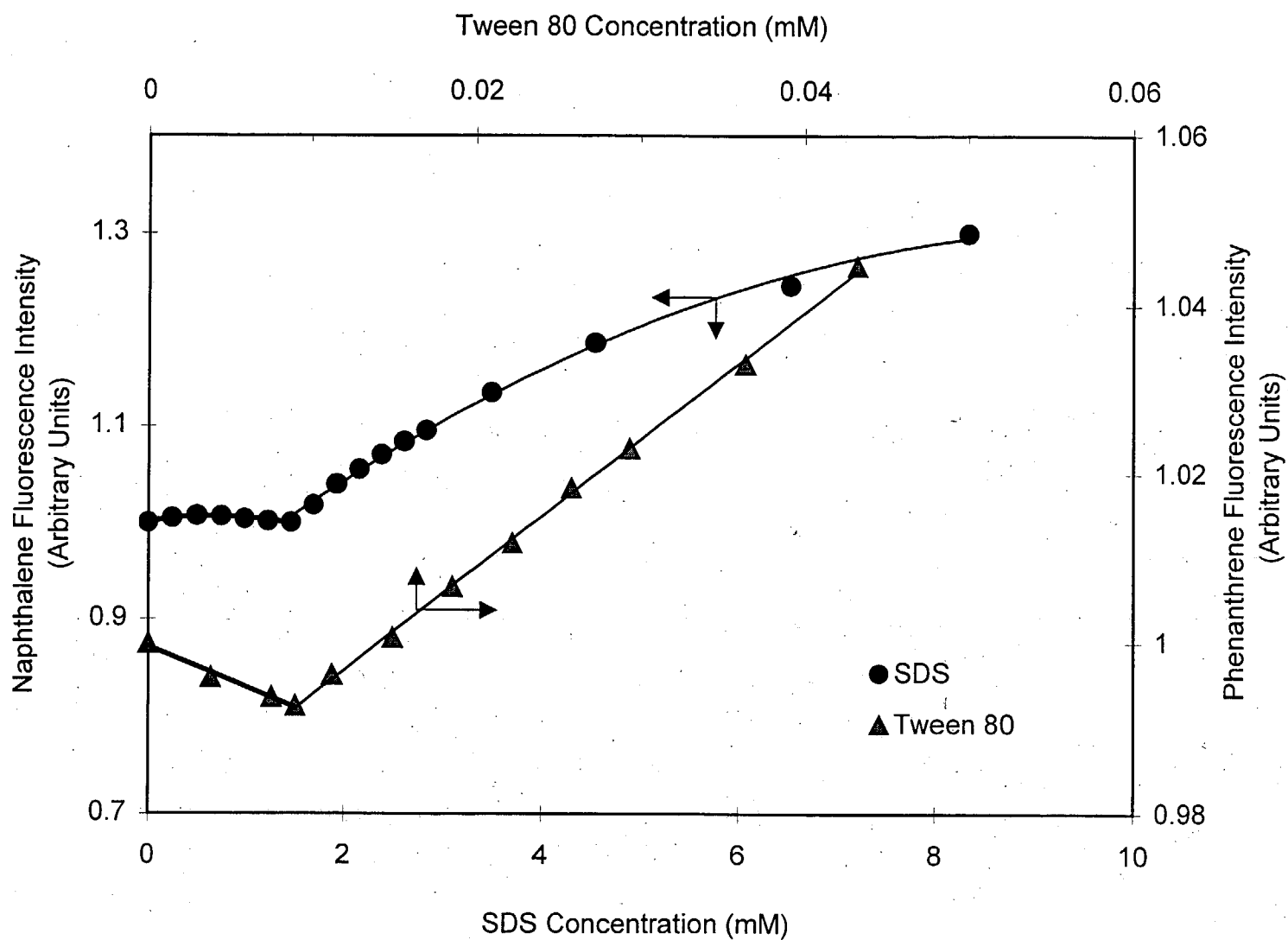


Figure 1. (Supporting Information)

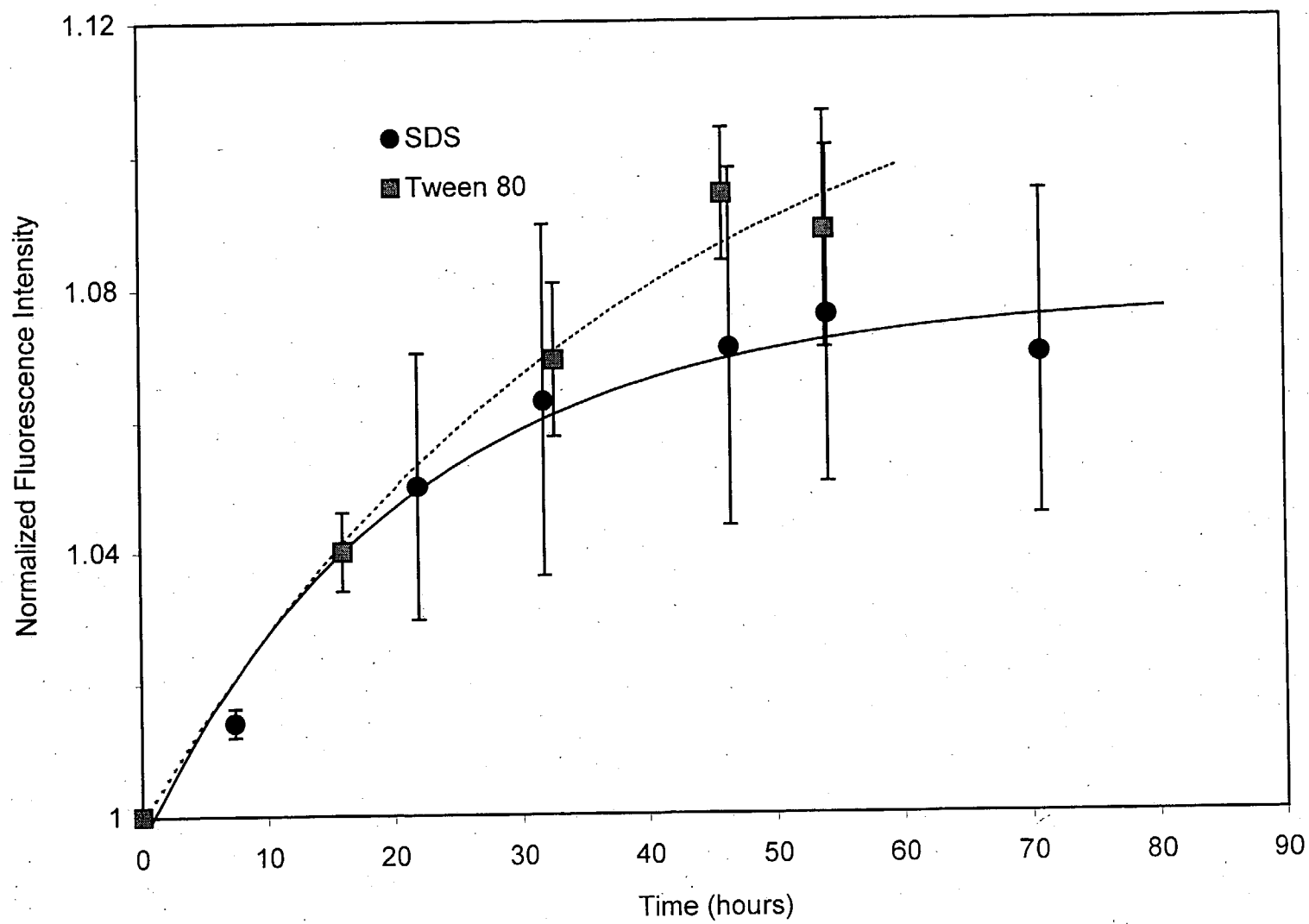


Figure 2. (Supporting Information)

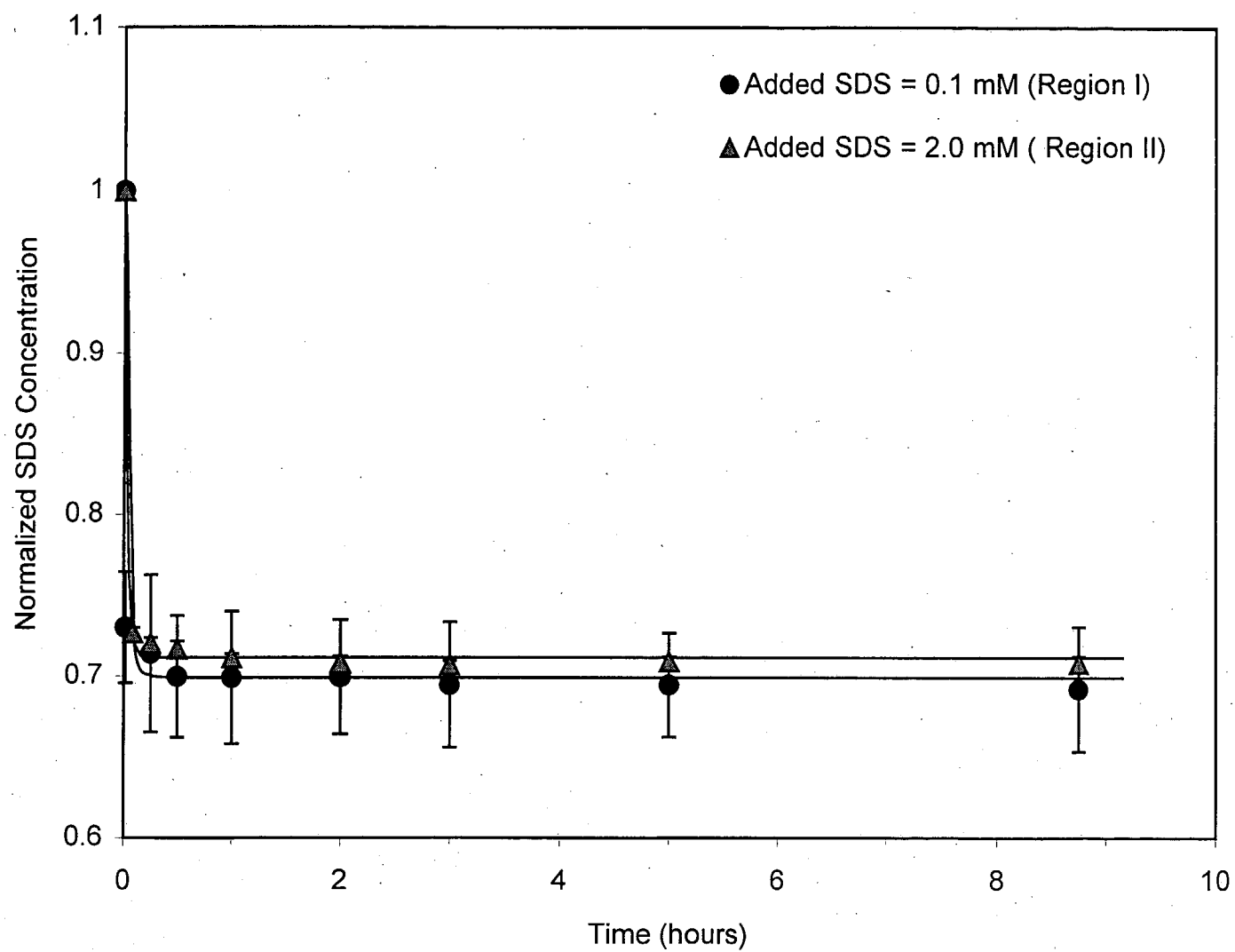


Figure 3 (Supporting Information).

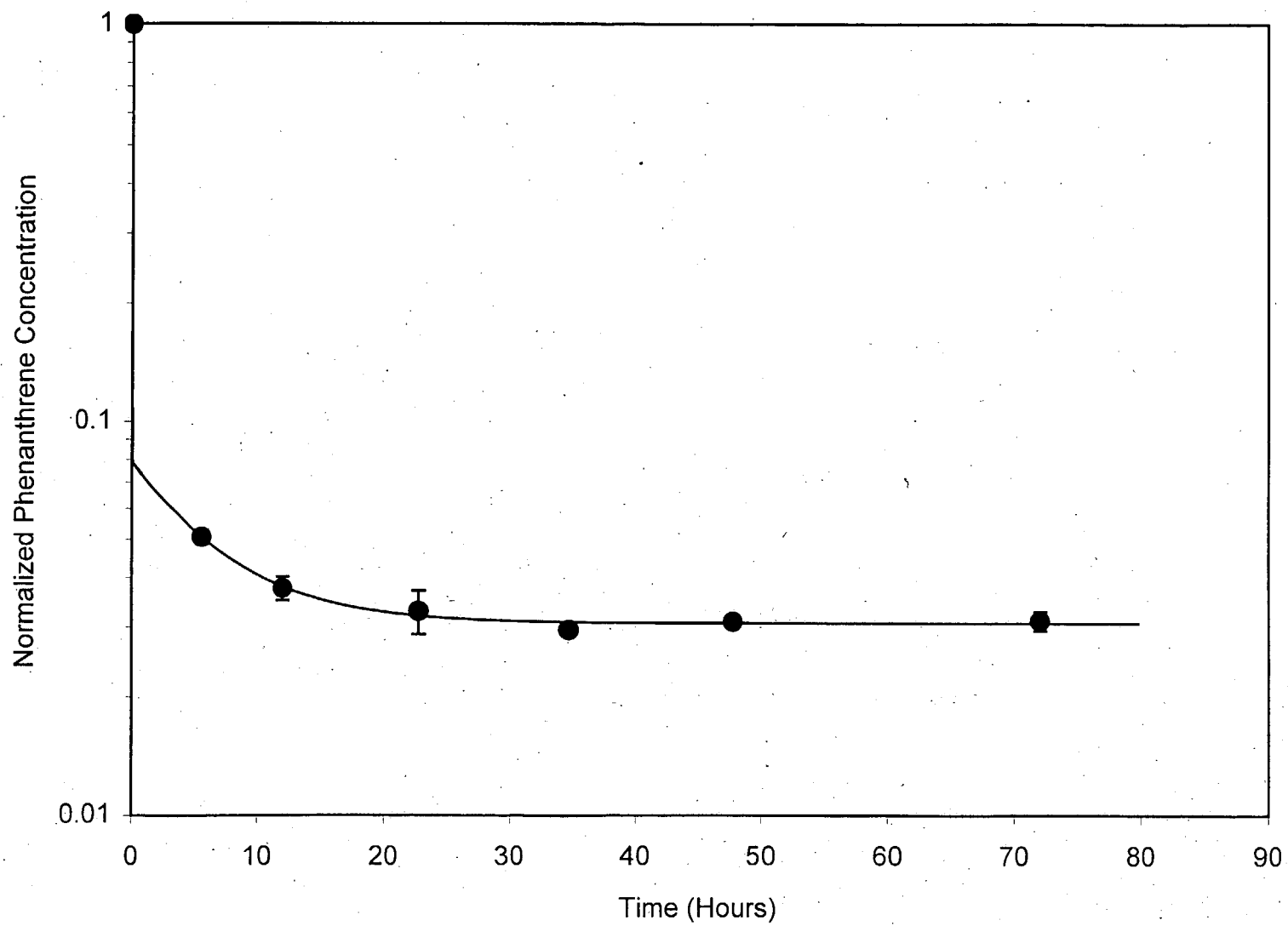


Figure 4 (Supporting Information).