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Using NMR Techniques to Find Partition Coefficients Across Biphasic Systems

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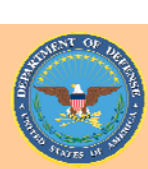*Department of Chemistry and Biochemistry, Boise State University*

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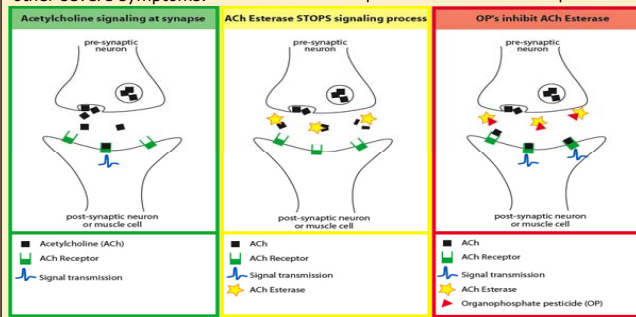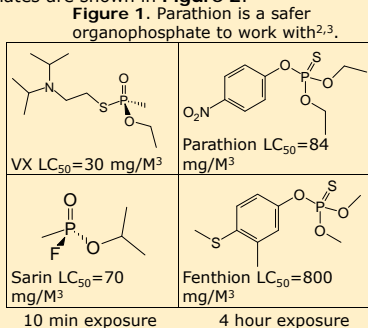
BOISE STATE UNIVERSITY

Abstract

A model biphasic system was studied using acetone in water and 1-octanol. The partition coefficient was found using z-axis single pulse slice-selective spatially resolved excitation (SPS3RE) nuclear magnetic resonance (NMR) spectroscopy. This SPS3RE NMR experiment allows for the collection of one-dimensional ^{1}H spectra at defined spatial intervals along the z-axis, providing analyte quantitation in both phases of the biphasic system. The concentration of acetone was characterized as a function of spatial location from the two-phase interface leading to the determination of partition coefficients by signal integration. This system was then expanded to analyze the hydrolysis of parathion in a biphasic system of parathion and deuterated water or sodium hydroxide with varying amounts of *tert*-butylammonium chloride. From this, the utility of a simplified, slice-selective pulse for analyzing heterogeneous samples is observed.

Introduction

- The decontamination of parathion (**Figure 1**) was studied with the help of a model biphasic system of water and 1-octanol.
- The two systems were investigated by SPS3RE NMR where "slices" between specific frequencies were analyzed.
- Decontamination incorporates two phases because the meniscus can optimize decontamination techniques. [1,2]
- The effects of organophosphates are shown in **Figure 2**.

Figure 2. Acetylcholinesterases catalyze acetylcholine in the brain (yellow panel). When organophosphates are ingested, they phosphorylate acetylcholine. This reduces the ability of acetylcholinesterase to degrade acetylcholine (red panel). This produces a large amount of acetylcholine present in the central and peripheral nervous systems. This may result in salvation, diarrhea, vomiting, gastrointestinal distress, and other severe symptoms. [3]

Figure 1. Parathion is a safer organophosphate to work with [2,3].

VX LC$_{50}$=30 mg/M^3

Parathion LC$_{50}$=84 mg/M^3

Sarin LC$_{50}$=70 mg/M^3

Fenthion LC$_{50}$=800 mg/M^3

10 min exposure   4 hour exposure

Acetylcholine signaling at synapse

ACh Esterase STOPS signaling process

OP's inhibit ACh Esterase

- Acetylcholine (ACh)
- ACh Receptor
- Signal transmission

- ACh
- ACh Receptor
- Signal transmission
- ACh Esterase

- ACh
- ACh Receptor
- Signal transmission
- ACh Esterase
- Organophosphate pesticide (OP)

NMR and MRI

- Apply magnetic field gradient across a sample. The resulting resonance frequencies can be described by a modification of the Lamor equation:

$$\omega = \gamma \,(B_0 + z \cdot G_z)$$

- With the sample spatially encoded, desired regions are excited by shaped radio frequency (RF) pulses.
- Combining RF bandwidths of 2 kHz and gradient strength of 4.51 G/cm.

Figure 3. Slices are selected by gradient encoding and a shaped RF excitation bandwidth. This can be used in MRI to look at various regions of the body (top) and adapted to HR NMR to look at discrete volumes within the sample.
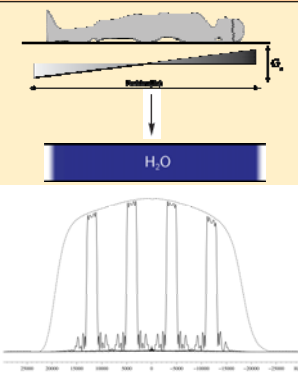
A Model System

- Integration of the acetone resonance at various distances from the meniscus of the mixture (also the center of the receiver coil) helped in determining the partition coefficients.
- These were found by taking the ratio of the integrals for symmetric slices about the coil center.
- Due to probe sensitivity and magnetic susceptibility effects, distances near the end of the coil window and near the interface provided inconsistent results.
- Optimal conditions were found between three and four millimeters from the coil center shown in **Table 1**.
- In **Figure 4**, one millimeter slices produced the spectra recorded. It provided adequate signal to noise with eight scans in a volume of 14.7 μL.
- Line shape is not a concern for the model system; integrations remain constant regardless of shim quality.

Table 1. Comparison of partition coefficients

Position (mm)	Experimental Log(p)		Literature Log(p)	
3	-0.204	0.019	-0.24	-0.1
4	-0.184	0.022		

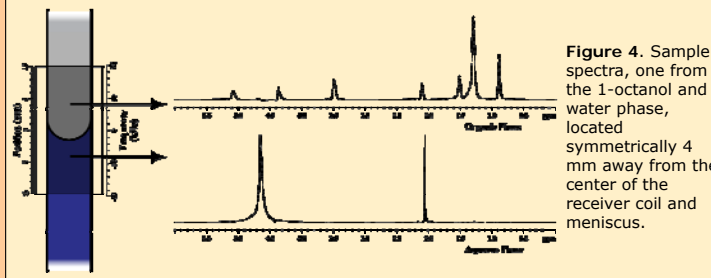Sangster, *J Phys Chem Ref Data* **1989**.

Figure 4. Sample spectra, one from the 1-octanol and water phase, located symmetrically 4 mm away from the center of the receiver coil and meniscus.

Practical System

- This technique has been expanded in preliminary studies to address a system consisting of CCl$_4$ and D$_2$O.
- *p*-Nitrophenol (pNP), a degradation product of parathion (PTH) hydrolysis was placed under saturating conditions in D$_2$O and allowed to diffuse into the organic phase shown in **Figure 5**.
- Integrations can be tracked as a function of position to monitor the presence of pNP in the organic phase.
- This can be used in future studies to monitor the hydrolysis rate under various conditions in a two phase mixture.

Figure 5. Pseudo-3D plot of pNP in D$_2$O and CCl$_4$ on a 500 MHz.
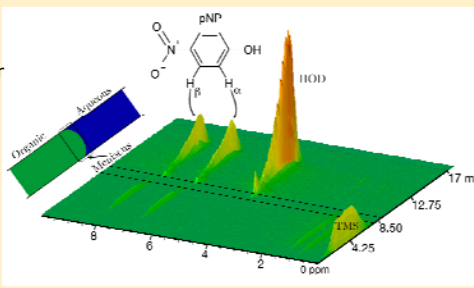
Experimental

H$_2$O and Octanol system

- 270 μL H$_2$O
- 240 μL 1-octanol
- 60 μL acetone

- Partition coefficients were calculated with the use of signal integration.

D$_2$O and CCl$_4$ System

- 275 μL D$_2$O
- 275 μL CCl$_4$
- 115 mM *p*-nitrophenol

- Relative concentration was tracked as pNP diffused across the interface.

Conclusions and Future Work

- Fast, single pulse experiment that can be done in a 4 hour lab time.
- Provides accurate partition coefficients.
- Limited by solvent properties: local gradients near interface should have similar magnetic susceptibilities.
- Nuclei dependent sensitivity and spin considerations.
- Kinetic studies of parathion hydrolysis.
- Monitor decontamination processes.

Acknowledgements

References

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