EXPERIMENT 1 – DETERMINING THE DIFFUSION IN LIQUIDS USING NMR: AN INTRODUCTION TO DATA & ERROR ANALYSIS

Jeff Yarger, Dept. Chemistry & Biochemistry, Arizona State University, Tempe, AZ 85287-1604. jyarger@gmail.com

Objective

In the first week, students will determine the diffusion coefficient for 1% chloroform ($CHCl_3$) in a solvent of d_6-acetone as well as the self-diffusion coefficient and viscosity of the solvent (acetone) and *all associated error* from the experimental NMR data and analysis process. Data will be provided to each student, therefore, the emphasis of this lab it not experimental technique. Rather, the goal of this exercise is to familiarizing yourself with <u>data and error analysis</u>. This is also an excellent opportunity to start getting familiar with computer analysis programs. In the second week, students will collect NMR diffusion data and be assigned a molecule (or specific NMR resonance) within a liquid mixture to determine the diffusion coefficient and *all associated error* from the experimental NMR data collected.

Introduction

Self-diffusion is the random translational motion of atoms, molecules or ions. Translational diffusion is one of the most fundamental forms of motion in liquids and gases, and is responsible for all chemical reactions (since the reacting species must collide before they can react). The diffusion of molecules in a liquid is also closely related to molecular size, as can be seen from the Stokes-Einstein equation [1-3],

$$D = \frac{kT}{f}$$

where *k* is the Boltzmann constant, *T* is temperature and *f* is the friction coefficient. For the simple case of a spherical particle with an effective hydrodynamic radius r_s in a solution of viscosity η the friction factor is given by

$$f = 6\pi\eta r_s$$

So, to first approximation this can be used to estimate the viscosity of a liquid from the measured self-diffusion coefficient.

The experimental data provided for this lab is pulsed field gradient spin echo (PFGSE) NMR spectra. This NMR method is one of the most direct and accurate means of measuring the diffusion coefficient of liquids. The technique was first described by E.O. Stejskal and J.E. Tanner in *Journal of Chemical Physics* (1965) [4]. The standard PFGSE pulse sequence is shown in figure
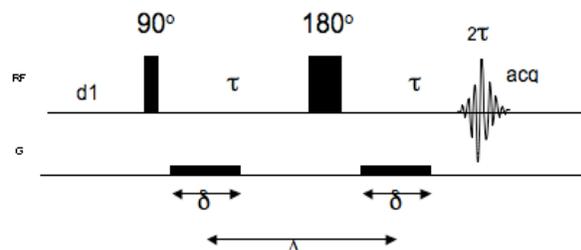

Figure 1 – Schematic of a standard pulsed field gradient spin echo pulse sequence. The top line is the RF channel and the second line is the gradient (G). The time between RF pulses is tau (τ), the time of the gradient pulse is δ and the time between gradient pulses is Δ. Lastly, d1 is the time between scans.

1. The top line labeled 'RF' is the pulses applied to the sample and represent a standard spin echo pulse sequence [5]. The second line is the gradient channel, G, and shows two gradient pulses that are turned on between the 90° ($\pi/2$) and 180° (π) RF pulses and between the π pulse and acquisition. The length of the two gradient pulses are the same and given by time δ. The time between the two gradient pulses is given by time Δ. The time between the 90° and 180° RF pulses is tau, τ. By repeating this pulse sequence with increasing gradient strength (stronger gradient pulses), the peak intensity of liquid state NMR resonances will decrease because of diffusion in the gradient field. The equation that describes this phenomenon was introduced by Stejskal and Tanner [4] and further explained in numerous scientific papers [6-8]. The derived result of using the pulse sequence shown in figure 1 is

$$\ln\left[\frac{S(2\tau)}{S(0)}\right] = -\gamma^2 G^2 D \delta^2\left(\Delta - \frac{\delta}{3}\right)$$

where $S(2\tau)$ is the signal at 2τ, $S(0)$ is the initial signal, γ is the magnetogyric ratio, G is the mangetic field gradient strength, D is the diffusion coefficient, δ is the amount of time the gradient pulse is 'on' and Δ is the time between the two gradient pulses. The signal S(0) is typically determined by run the experiment with any gradient pulse power (G=0%). The signal S(2τ) is acquired directly in the experiment. Hence, these parameters are determined directly from NMR experiments and corresponding data. The magnetogyric ratio (or gyromagnetic ratio) of a nuclei is a ratio of its magnetic dipole moment to its angular momentum. This is a constant for each nuclear spin isotope [2]. The gradient is controlled by the NMR and is calibrated to provide a known gradient typically expressed in Telsa per meter (T/m) or Gauss per centimeter (G/cm). The timing parameters, δ and Δ must be experimentally set. With all these parameters set and/or measured, you will be able to use this equation to determine the diffusion coefficient of a liquid from a set of PSFSE NMR measurements.

The NMR data for this lab will be provided. Hence, the focus will not be on understanding the NMR experiment, but rather on understanding common techniques to process data and determine the error associated with experimental measurements. All experimental data that you will acquire in physical chemistry lab will need to be 'analyzed' and reported with an associated 'error'. There are numerous books that cover data and error analysis [e.g. 9] and a separate handout on introducing this topic is provided on the class website. Experimental data **always** has inaccuracies. Therefore, in using the numbers that result from experimental observation, it is necessary to know the extent of these inaccuracies.   If several observations are used to compute results, one must know how the inaccuracies of the individual observations contribute to the inaccuracies of the result. This lab is designed to allow students to focus on learning common data and error analysis techniques.   These techniques will be used on all future experimental labs.

Experimental

The first week of this experiment you will be given experimental data and your objective is only to analyze this data and determine the associated error. The data is available on the course website. If you have problems getting the data off the web, a TA can email the data to you. The data you will be given is NMR processed spectra. This data was chosen because it contains most of the elements you will need throughout the semester for data fitting and error analysis. The data is stored as a zip file. The archived zipped spectra files are split into separate ASCII files with the names being CHCl3_in_Acetone_d6_Grad#.txt, where the number (#) indicates the percent strength of the gradient.   Only the real spectra are provided (no imaginary data provided).   So, for example, if you wanted the spectrum of the 15% gradient data set, the filename would be CHCl3_in_Acetone_d6_Grad15.txt.   The data files provided are ^{1}H NMR

spectra of 1% $CHCl_3$ in d_6-acetone at 25℃ using a pulsed field gradient spin echo (PFG-SE) pulse sequence described in the introduction. The PFG-SE NMR data (spectra) were taken at several gradient strengths. Specifically, we took data at gradients of 2, 15, 29, 42, 55, 68, 82 and 95 %. These percent gradients can be converted to an absolute gradient strength by calibration, using a liquid sample of know diffusion coefficient. This is typically the solvent or a sample of water.

1 ml of a 1% $CHCl_3$ in 99.5% d_6-acetone (perdeuterated, Aldrich) was placed in a standard 5mm glass NMR tube. ^1H (proton) NMR data was collected on a 400 MHz Bruker Avance NMR. The spectral width was set to 3816.79 Hz (9.5453 ppm) and the spectral frequency is 399.8575 MHz. The ^1H PFGSE NMR data was acquired with percent gradients of 2, 15, 29, 42, 55, 68, 82 and 95 % for a sample of 1% CHCl3 in d_6-acetone at 25℃. For all experiments, the value of δ=0.8 ms ± 100 ns and Δ=200 ms ± 100 ns. The raw data consists of free induction decays (FID) that have been Fourier transformed to spectra. The resulting spectra are saved in ASCII format. By extracting the peak area and/or peak height at various magnetic field gradient strengths, one can use the above Stejskal and Tanner equation and a linear least squared fitting routine to extract the diffusion coefficient, D. To calculate the viscosity, one only needs to apply the Stokes-Einstein equation, as discussed in the introduction. The magnetogyric ratio or gyromagnetic ratio (γ) is a constant for all isotopes and can be found in tables of nuclei properties [2,10]. The ^1H gyromagnetic ratio (γ) is reported on wikipedia at http://en.wikipedia.org/wiki/Gyromagnetic_ratio. Remember, when using this constant to ensure whether or not you are in angular units, radians.

For the second week, a mixture of several compounds will be made an put in an NMR tube for the class. Students will collect NMR data to allow the determination of each compound diffusion coefficient. The data will be collected by students with the help of TA's that are familiar with the NMR spectrometers. Each student will be assigned a specific resonance or compound to determine the diffusion coefficient.

Data Analysis

Determine the diffusion coefficient of $CHCl_3$ in d_6-acetone. Also determine the viscosity of the solvent at 25℃ from the provided NMR spectra. An outline of the steps needed to take these NMR spectra and use them to calculate the diffusion coefficient is given below:

- Download the NMR data from the web. All data is in ASCII format. You should have PFG-SE NMR data (spectra) of 1% $CHCl_3$ in d_6-acetone at 2, 15, 29, 42, 55, 68, 82 and 95 % gradients.
- Read the data into a data analysis package such as Kaleidagraph, Excel, Origin, SigmaPlot, DeltaGraph, Octave, Mathematica, Scilab or Matlab. Make a stacked plot of the spectra (for your report it is common to use a subset of the data to keep the plot clear and not too cluttered).
- Determine the signal intensity for each spectral element, $S(2\tau)$ and its associated error (estimation of error). The signal strength can be determined from the area under the peak in the NMR spectrum or from the height of the NMR peak, assuming the linewidth is constant.
- Using the $S(2\tau)$ data of the solvent (or calibration standard) and the known self-diffusion coefficient of the solvent or a separate calibration standard sample (typically H_2O/D_2O, because it's diffusion rate is so well known), you can convert all % gradients into an actual magnetic field gradient in T/m or G/cm. This is done using the Stejskal-Tanner equation.

- Looking at data in a linearized fashion can help to determine if any data looks out of place and is suspect of being 'bad' data. If so, use should use a Q-test to determine whether the data can be omitted (rejected).
- Now you can use the Stejskal-Tanner equation to determine the diffusion coefficient, D, of the assigned solute (or any peak in the NMR spectrum). This is typically done by plotting the natural log $S(2\tau)$ versus the gradient strength squared (G^2). Remember to propagate errors.
- Use the Stokes-Einstein equation and an estimate of the hydrodynamic radius of the solvent (this can be done using Gaussian/GaussView) to calculate the viscosity. Again, remember to propagate errors from the individual variables.
- Compare the calculated viscosity and diffusion coefficient to literature values.
- Done! Now wasn't that easy?
- ***In week 2 of this lab, we will go to the NMR lab (ISTB1 L2-63) and collect another set of NMR data. The same procedure as described above can be used to analyze the data and determine the diffusion coefficient. Report the diffusion coefficient for the solvent and <u>assigned</u> solute.***

Safety

Magnetic safety will be discussed immediately before the NMR lab (during week-2). I don't thing that computers pose much health risk. However, they can cause mental anxiety.

References

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