ATR-FTIR spectroscopy study of hydrogen bonding trends, Physical Chemistry Lab #2

Hydrogen bonding is a central aspect of molecular interactions in chemistry ranging from biochemistry to materials science. In this laboratory experiment we will use vibrational spectroscopy measured in by attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy.

2.1 Introduction

Hydrogen bonding between phenols and amides to form 1:1 and 2:1 hydrogen bonding complexes has been previously described in the literature.[2] In order to determine the strength of interaction between two molecules one would prefer to have pure 1:1 bonding complexes. In this lab we will assume that the 1:2 hydrogen bonding complexes are a minor component and do not interfere with the observations. IR spectra of the phenol-amide hydrogen bonding complexes reveal a shift in the stretching frequency of the amide carbonyl group (Figure 2.1).[2] The magnitude of the shift is dependent on the identity of the phenol.

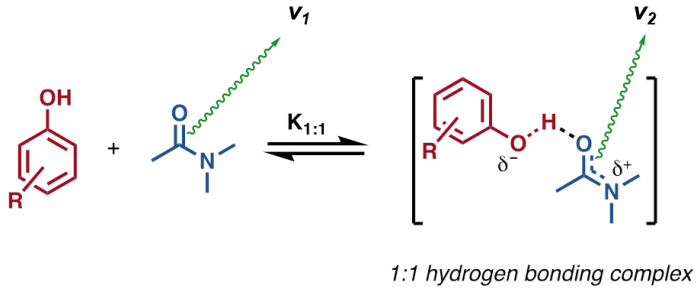


Figure 2.1. Diagram of the formation of a 1:1 hydrogen bonding complex between a phenol and an amide. The stretching frequencies of the uncomplexed and complexed amide are designated v1 and v2.

Figure 2.1 shows the target molecules studied in this laboratory experiment, N,N-dimethylacetamide (DMA) and a series of substituted phenols. We will explore the relationships between phenol pK_a, the Hammett values for the phenol substitutions (σ), amide carbonyl stretching frequencies, and hydrogen bonding complexation energies.

2.2 Experimental

The experiments will be carried out on a Bruker single reflectance ATR FTIR instrument. Each sample should be measured by a minimum of 16 scans from 400 cm^{-1} to 4,000 cm^{-1} with 4 cm^{-1} resolution. We will use the following phenols were used in the experiments: 4-chlorophenol, 4-bromophenol, 4-methoxyphenol, 4-cyanophenol, 4-nitrophenol, and para-cresol (4-methylphenol). These molecules will be dissolved in toluene with DMA added to create solutions that can be deposited on the ATR-FTIR element for measurement. Measurements should be made quickly to avoid losses of solvent due to evaporation. Evaporation is unavoidable in the experimental configuration used and is one of the sources of systematic error in this experiment.

2.2.1 Sample preparation

1. Make solutions with the following phenols; 4-nitrophenol, 4-cyanophenol, 4-methoxyphenol, 4-chlorophenol, 4-bromophenol and phenol. Make solutions by weighing out *ca.* 100 millimoles of each phenol and then dissolving the phenol in 5 mL of toluene. For example, for phenol this would be 94 mg of sample added to a 5 mL volumetric flask followed by addition of toluene solvent up to the mark. The para-phenol solutions are then added to 10 mL volumetric flasks. Add 0.25 mL of N,N-dimethylacetamide (DMA) to each 10 mL volumetric flask containing the phenol solution, and dilute to 10 mL with toluene. Note that DMA is a liquid and you may dispense the neat liquid using a syringe. Five drops of a sample

solution, delivered with a glass Pasteur pipette, is then added to the ATR crystal and the measurement is immediately started. These samples were not used for equilibrium studies. You should also measure the frequency of DMA by itself without any phenol. However, in each of the above mixtures, there will likely be an equilibrium such that there is some free DMA and some bound DMA, which has a frequency shift due to hydrogen bonding with the respective phenol.

2. For binding/equilibrium studies of 4-chlorophenol, the general procedure described above was employed with the exception that *ca.* 0.200 moles of 4-chlorophenol should be weighed and diluted in a volumetric flask to make a 10 mL stock solution. Various volumes of this solution ranging from 0.1 mL to 5 mL will be added to 10 mL volumetric flask, 0.25 mL DMA is added the solution is diluted to the mark. Thus, the concentration of DMA is held constant and the concentration of 4-chlorophenol binding is changed over a factor of 10 to cover an important range of binding. For example, the 10 mL stock solution can be added in the following volumes, 0.1 mL, 0.2 mL 0.3mL 0.5 mL 1.0 mL, 3.0 mL, 5.0 mL.

2.2.2 Comparison of frequency shifts due to hydrogen bonding

The shift in the DMA carbonyl stretching frequency (Δv) is defined as:

$$\Delta v = v_{uncomplexed\ DMA} - v_{complexed\ DMA} \quad (1)$$

The value obtained for the carbonyl stretched of uncomplexed DMA is 1660 cm^{-1}, and is in accordance with literature reports (although in different solvents).[2] Typical values for the carbonyl stretches of DMA complexed with various phenols ranged from 1625 cm^{-1} to 1633 cm^{-1}, giving Δv values of 27-35 cm^{-1}. Δv measurements are taken from the wavenumber that gives the maximum peak height for the desired peak (figure 2).

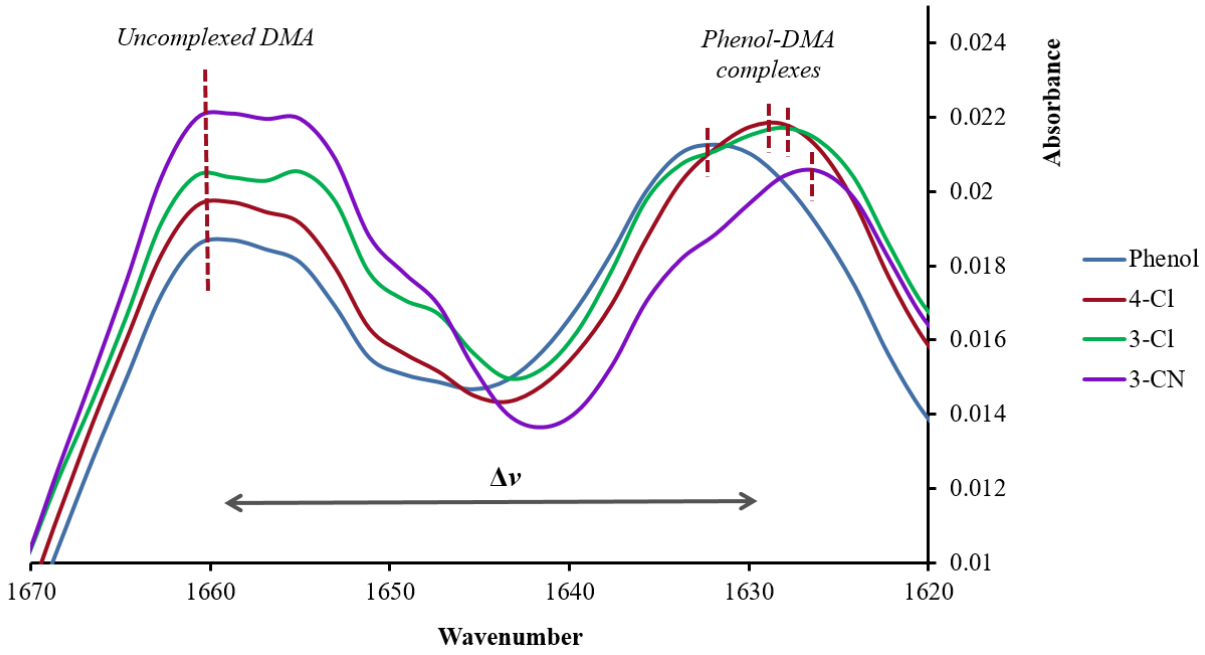


Figure 2. Typical FTIR spectra of DMA/phenol mixtures observing the shift in the carbonyl stretching frequency between DMA and select DMA-phenol complexes.

2.2.3 Equilibrium binding study

Given the following equilibrium:

$$DMA + Phenol \rightleftharpoons 1{:}1\ Complex \tag{2}$$

We have the following:

$$K_{1:1} = \frac{[AP]}{[A][P]} \tag{3}$$

where $K_{1:1}$ is the association equilibrium constant for the formation of the 1:1 phenol-amide complex, [AP], [A] and [P] are the concentrations of the complex, amide (DMA), and phenol, respectively.[2] Assuming the ratio of concentration of the complex to the sum of the concentration of the complex plus the concentration of amide is proportional to the ratio of their absorbances, we may write:

$$\frac{[AP]}{[AP] + [A]} \approx \frac{\mathrm{A}_{AP}}{\mathrm{A}_{AP} + \mathrm{A}_{A}} \equiv \frac{\mathrm{A}_{AP}}{\mathrm{A}_{T}} \tag{4}$$

Re-writing in terms of equilibrium constant and phenol concentration, we have:

$$\frac{\mathrm{A}_{AP}}{\mathrm{A}_{T}} = S\frac{K_{1:1}[P]}{1 + K_{1:1}[P]} \tag{5}$$

where S represents a scaling coefficient. Ideally, S would have the value of one; however, this arises from when the ratio of concentrations is equal to the ratio of the absorbances. The value of S may deviate from one because of experimental factors such as baseline corrections or absorbance from interfering species.

The absorbance for a given peak may be obtained from maximum absorbance for that peak. However, the peaks are overlapping in this case and that way of estimating the intensity has a potential error. Fitting the peaks of A_{AP} and A_A is a more accurate way to obtain the relative populations of molecules in each configuration (hydrogen-bonded and non-hydrogen-bonded). You may use a model with two Gaussian functions to fit the data and thereby to obtain an estimate for the relative concentration in each configuration. Irrespective of the method used to obtain the absorbance, A_{AP}/A_T is plotted as a function of phenol concentration to obtain the experimental function given by Eqn. 5 . The absorbance data may then be fit to the equation using non-linear least squares fitting with $K_{1:1}$ and S as parameters. Non-linear least-squares fitting can be implemented in Excel using the Solver function.

2.3 Analysis

2.3.1 Application of the Hammett equation

The Hammett equation provides a linear free-energy relationship that relates reaction rates and equilibrium constants for reactions involving benzoic acid derivatives. Specifically, meta- and para-derivatives are classified in terms of their electron donating or withdrawing capability and these inductive effects are quantified with two parameters: a substituent constant and a reaction constant. The equation published by Louis Plack Hammett in 1937.

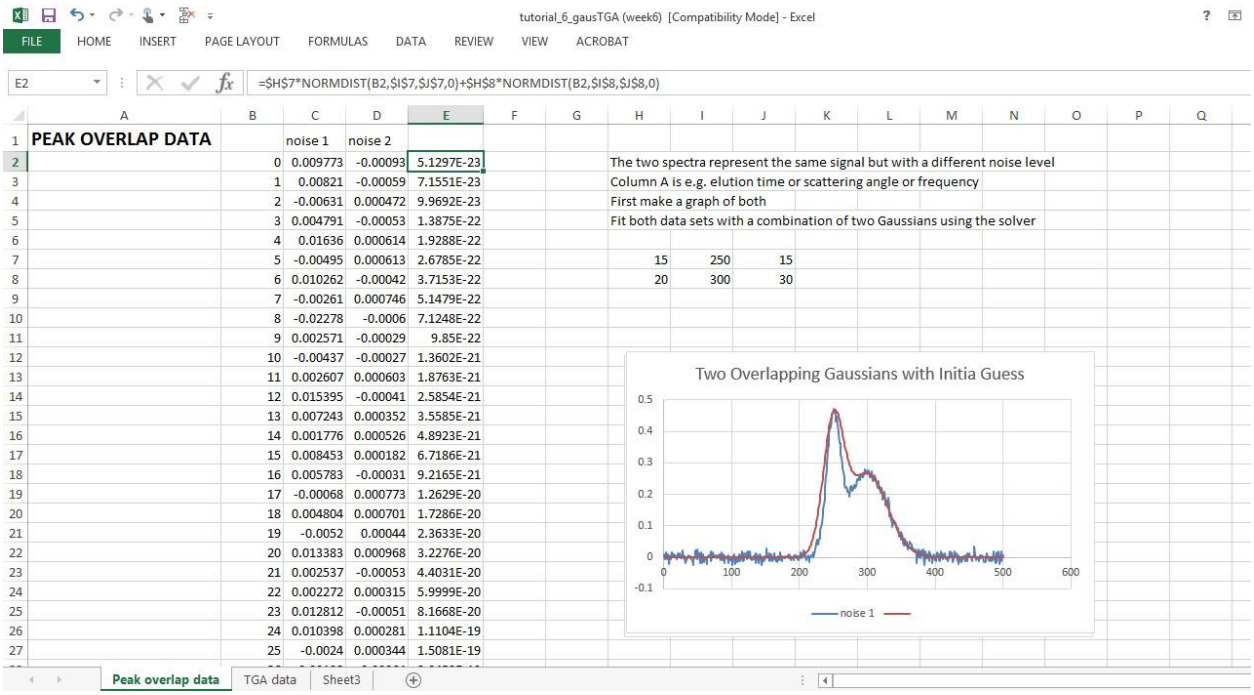
The basic idea is that for any two reactions with two aromatic reactants only differing in the type of substituent, the change in free energy of activation is proportional to the change in the Gibbs free energy. The Hammett equation is

$$\log\frac{K}{K_0} = \sigma\rho$$

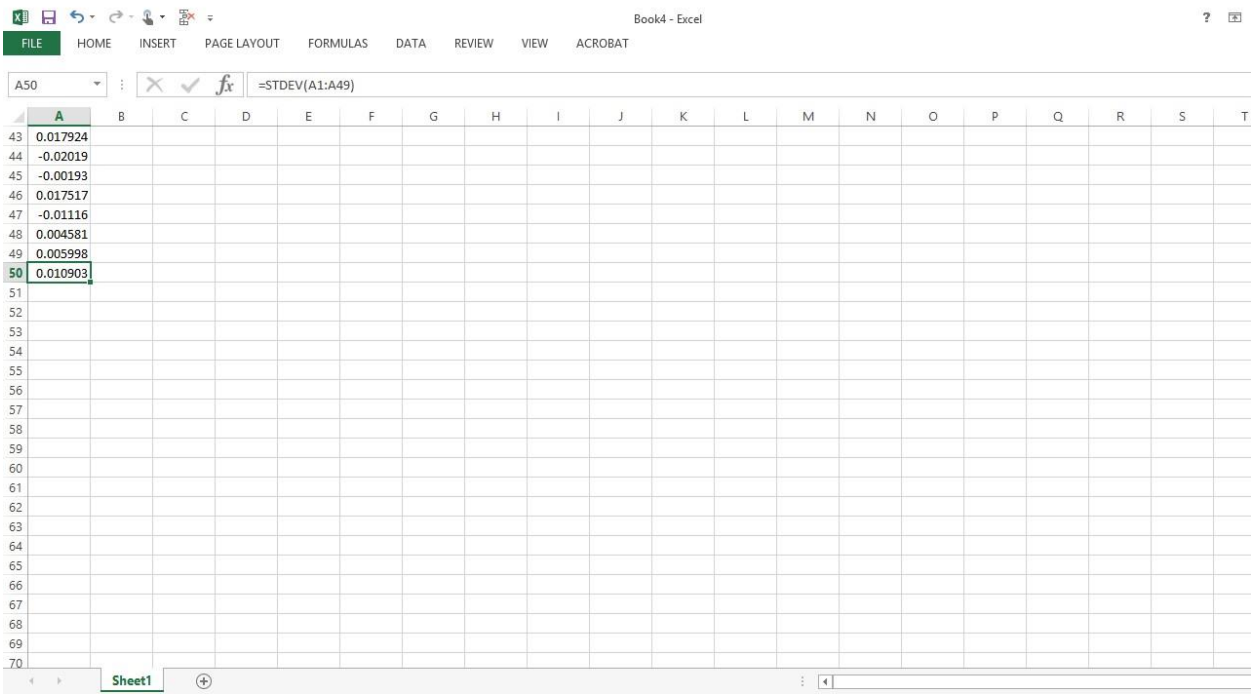
The equilibrium constant K in a benzoic acid with a substituent (e.g. chloro-, fluoro-, nitro-, methyl- etc.) is related to the reference equilibrium constant, K_0, when hydrogen is the bonded atom. The σ depends on the substituent and has a tabulated value. The ρ constant depends on the type of reaction. Although these relationships were derived for benzoic acid, subsequently they have been used for a wide range of aromatic compounds, including phenols. The reaction can be loss of H^+ and therefore the σ constant relates to K_a of the acid. This relationship can also apply to reactions such as hydrogen bond formation as described above in this laboratory.

2.3.2 Gaussian fitting using the non-linear least squares method

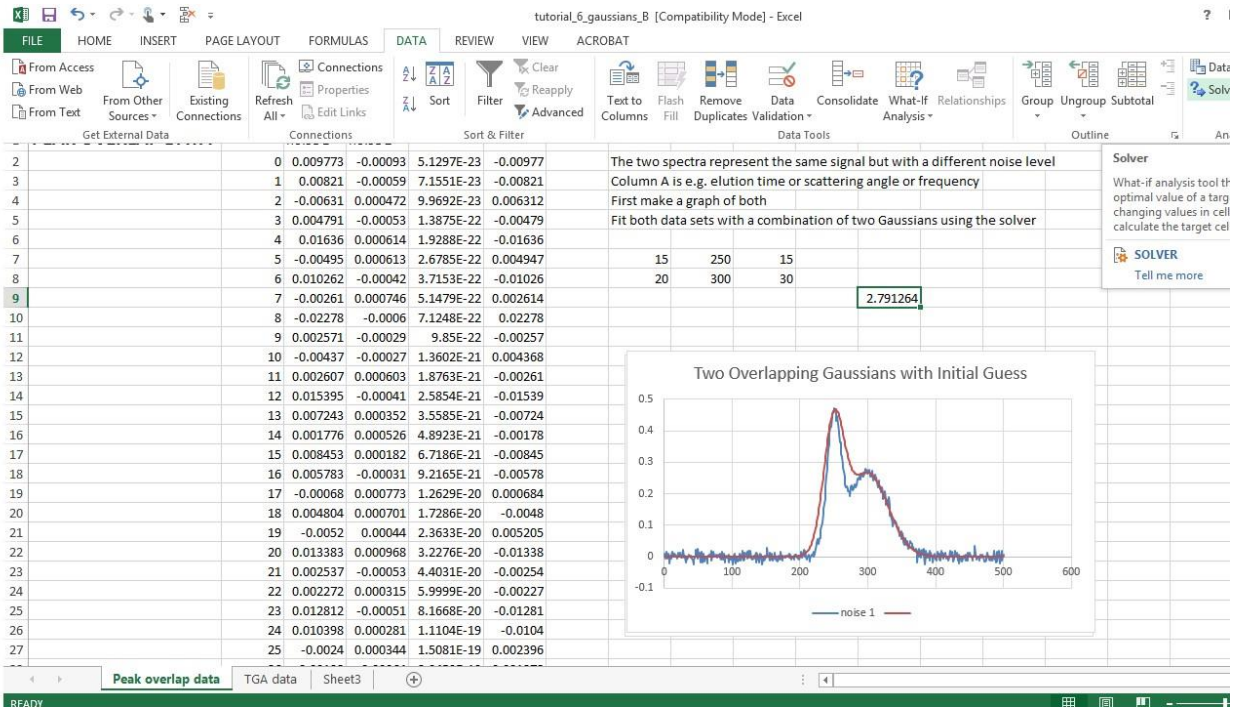
This section give an example of how to use Excel to calculate the non-linear least squares fit to two Gaussians.



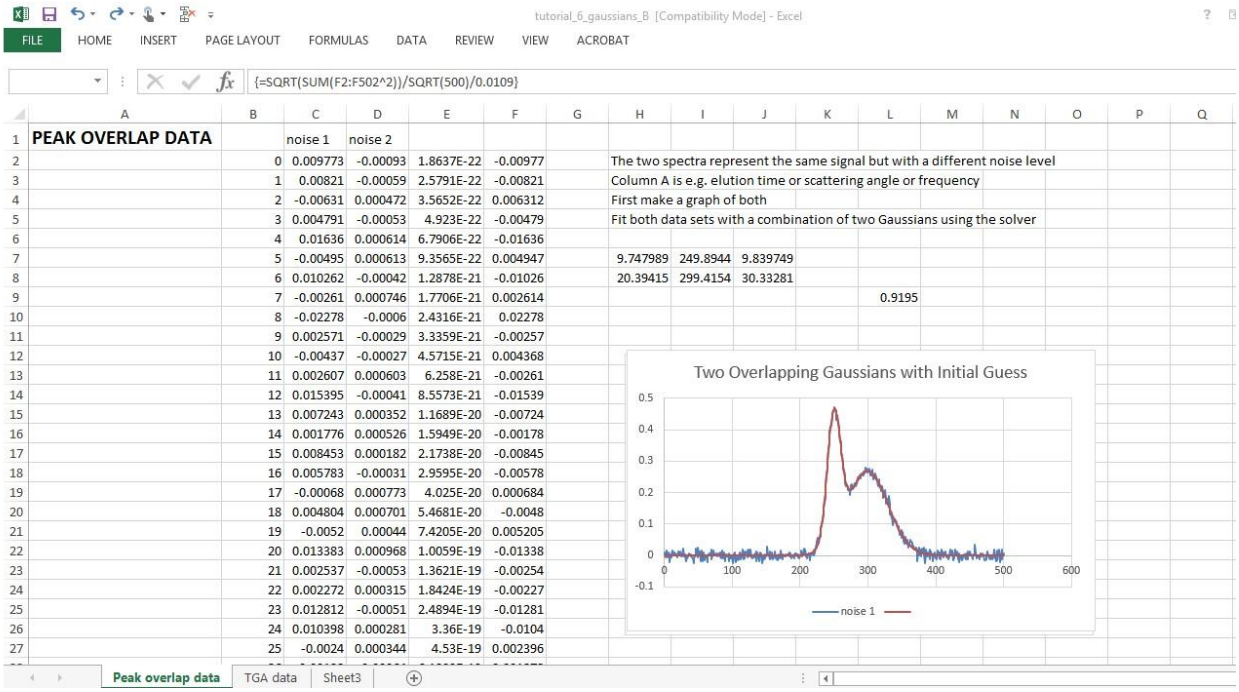
Estimate the noise in the data by taking the standard deviation on a flat region of the data. This is basically a 1-D application of RLS if want to use the full power of that worksheet (including elimination of outliers). You are not likely to have outliers in the data that you have obtained. You may also the STDEV function in Excel on the selection region. This is shown on the next slide.



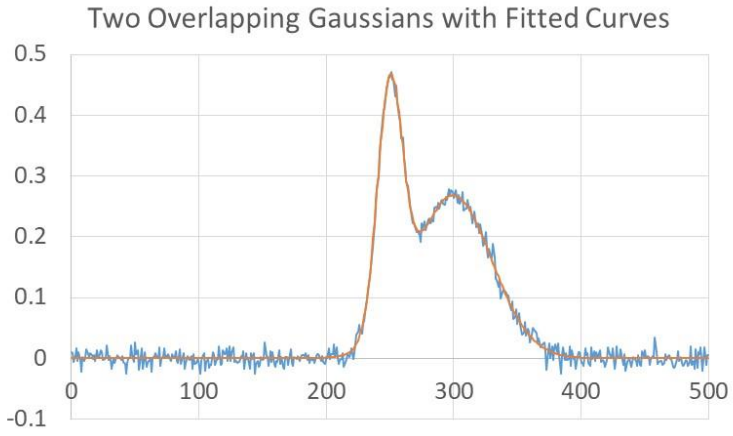
Define the value of chi-squared (χ^2) in cell L9 on the following figure.



Here we see that the χ^2 value is greater the one initially, i.e. before we start the iterative process of non-linear least squares fitting.



After application of Solver we obtain a fit to the two exponentials that has a $\chi^2 < 1$. You need an accurate estimate of the noise to obtain a good value of χ^2.



Amplitude	Position	Width
9.75	250.0	9.84
20.4	299.0	30.3

2.4 Laboratory Report

The report should present an analysis of the two types of data obtained, the frequency shifts obtained for various phenols and the equilibrium constant obtained from a series of 4-

chlorophenol concentrations. The series of frequency shifts can be plotted vs. the Hammett σ parameter or even the pKa of the phenols. The pKa also should be correlated with the Hammett σ parameter, which is one reason why the latter correlation should provide a linear relationship. It should be born in mind that the pKa is determined in water, while the solvent used in this experiment was toluene. Nonetheless, the electron-withdrawing or donating character of the para substituent in the phenol plays an analogous role in each of these observations.

The band shifts obtained for various phenols can be obtained by estimation of the peak position of the of the carbonyl stretch of DMA in pure toluene solvent compared to the shifted value in the presence of various concentrations of phenol. Care must be taken to account for the possibility that the band shift is not complete and also for the possibility that some population of hydrogen bonding involves a double hydrogen bond to two of the lone pairs on the carbonyl. Gaussian band fitting should be attempted although this may prove difficult to use depending on the exact line shapes. You can also use the absorbance maximum estimated graphically to calculate the shift. But, please report the results of Gaussian fitting and any issues that you encounter. These aspects of the problem are suitable for the Discussion section.

The equilibrium data can be plotted as a function of the fraction bound vs. the phenol concentration. The fraction bound is determined from the area under the curves of the A and AP FTIR bands. The fit to two parameters described above gives an estimate of the equilibrium constant. An equilibrium constant in turn gives the free energy of the reaction, which in this case is the formation of a hydrogen bond. Here too, Gaussian fitting (to a two Gaussian model at a minimum) is needed. You will need to perform a baseline correction and to use a normalized Gaussian (or calculate the area after the fact). However, the difference peak heights can also be estimated from the difference in absorbance at the maximum wavenumber, $\tilde{\nu}_{\max,}$ of each band. Even if you decide to use the latter method for quantitative analysis, please report the results of Gaussian fitting. Possible sources of systematic error and the limits of precision due to non-random factors that enter into the experiment should be discussed in the Discussion section. All plots should be presented with an appropriate error analysis. Two types of fitting are involved, linear least squares for the first part and non-linear least squares for the second part.

References

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