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Acidity and basicity measurements were made on some silicone stationary phases that are used in gas chromatography. These measurements were obtained by both gas chromatographic and nuclear magnetic resonance spectroscopic means. The gas chromatographic measurements were obtained by chromatographing a probe pair on each stationary phase. For acidity measurements butylamine/butylchloride was the probe pair and for basicity measurements the probe pair ethanol/acetone was used. The relative retention time of each probe pair on each stationary phase was used as the measure of acidity or basicity. Correlations between the relative retention time and actual acid or base strength were then made by the use of NMR. Nuclear magnetic resonance measurements were made using a modified version of the Benesi-Hildebrand equation $1/\delta_{obs} = \frac{1}{[B]} \cdot \frac{1}{K\delta_c} + \frac{1}{\delta_c}$ which requires that a 1:1 hydrogen bonded complex between an acid and a base be formed. Where [B] is the base concentration, K is the equilibrium constant and δ_{obs} and δ_c are the

observed and the complexed chemical shifts. By varying the concentration of the base and measuring the chemical shift of the hydrogen bonded proton, linear plots were obtained. Results, in the form of equilibrium constants, were then obtained from the slope of the plots. For acidity measurements the stationary phase was the acid and quinuclidine was the base. For basicity measurements the stationary phase was the base and chloroform was the acid. The end result of these measurements was to lay the groundwork for a different scheme for the classification of gas chromatographic liquid stationary phases which would be easier to use than any classification scheme that is available today.

Acidity and Basicity Measurements of Some Silicone Gas Chromatographic Liquid Stationary Phases

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Typed by Opal Grossnicklaus for Gary J. Miller

To family and friends,
whose support and
encouragement made
this work possible.

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CHAPTER 1

INTRODUCTION

One of the more important decisions to be made by today's chromatographer is the selection of a liquid stationary phase. Considering the hundreds of stationary phases on the market today it's no wonder that decisions about choice of phase are usually made from experience. A large part of the separation problems can be solved by the chromatographer who can rely on experience and intuition to "decode" the published stationary phase classification schemes. Unfortunately, since gas chromatography is such a good separation method, many researchers outside the field have a need for a working knowledge of the technique. Those chromatographers with little or no experience must learn through time consuming trial and error.

To aid the chromatographer many attempts have been made to develop classification schemes for liquid stationary phases. Most notable among these are the work of Kovats,[1-4] Rohrschneider,[5,6] and McReynolds.[7,8] Unfortunately these classification schemes require a considerable amount of judgement and chemical intuition since most of their parameters contain information about more than one type of interaction.

To simplify the classification schemes each of the major types of interaction (dispersion, polarity, acidity, basicity) should have its own parameter which does not contain any contribution from the other types of interaction. Only a small amount of chemical intuition would be necessary to use this type of classification scheme. This would open up the field of chromatography to those who have need of the technique but can't afford to spend the extra amount of time to find a proper stationary phase by trial and error methods.

It has long been known that the factors that influence the separation of solutes with very similar properties are the chemical interctions between the stationary phase and solute molecules. Even though these interactions have been considered they have for the most part been left unstudied. The bulk of the investigations into the causes of chromatographic separation have simply classified stationary phases into various categories of polarity. In doing this they have combined other interactions, such as acidity and basicity, into the polarity parameter. These approaches can be more easily understood if it is remembered that:[9,10]

a) Gas chromatography is such an efficient separation technique that knowledge of the individual interactions concerned with the separation process is not a prime necessity;

b) The selective interaction in question may be unknown or it may be the result of a number of simpler interactions that cannot be individually evaluated;

c) The exact composition of a great number of stationary phases is not known (this is so for those polymers that show stability at high temperatures).

As the number of chromatography applications increases, more difficult separations are being encountered. The need to separate isomers as well as other compounds which possess very similar chemical and physical properties has inspired research in the area of the specific interactions taking place between stationary phase and solute molecules. To get a better feel for the direction the research on these interactions is taking, it may be helpful to provide some background to see what direction the research has come from.

CHAPTER 2

GAS CHROMATOGRAPHIC APPROACH

In 1958 Kovats[1] developed a retention index system which would allow a chromatographer to know approximately where a solute would elute relative to the homologous series of n-alkanes. The series of n-alkanes was given a retention index which depended on the number of carbon atoms present in the molecule. Methane, having one carbon atom, has a retention index of 100; ethane, 200; propane, 300; etc. The retention index of a solute which elutes between ethane and propane on a chromatogram would therefore be between 200 and 300. The retention index of a solute (x) can be calculated from the specific retention volume (V_g) using the following equation

$$I = 100 \frac{\log V_g(x) - \log V_g(P_z)}{\log V_g(P_{z+1}) - \log V_g(P_z)} + 100_z \qquad (1)$$

where z is the number of carbon atoms and P_z and P_{z+1} are the n-alkanes that elute before and after the solute on a chromatogram. The specific retention volume is directly related to the retention time so that equation 1 can be simplified to:

$$I = 100 \frac{\log t_s(x) - \log t_s(P_z)}{\log t_s(P_{z+1}) - \log t_s(P_z)} + 100_z \qquad (2)$$

where t_s comes from $t = t_s + t_m$; t being the total retention time from the time of injection, t_s is the sorbed time which is the amount of time the solute spends in the stationary phase, t_m is the mobile, dead, or unretained time which is the amount of time that the solute spends in the mobile phase being carried through the column. To measure the retention index of any solute on any stationary phase one only needs to measure the retention times of the solute and the proper n-alkanes. Large tables are available containing retention index data for many different solutes on a large variety of stationary phases at several temperatures.

This system becomes a little more complicated when one wants to determine what stationary phase should be used to separate two solutes which have similar properties. The retention index of the two solutes must be found on various stationary phases in the data tables. In order for there to be proper separation there must be a retention index difference of about 50 units. Until the difference of 50 units is found more and more stationary phases must be looked up. In effect these tables of retention index data simply report the results of other chromatographic researchers.

There are several advantages to this approach which originally made it popular. The retention index is similar

to the relative retention time in that it is independent of flow rate, amount of stationary phase, or the length of the column. The index is linear since the log of the retention times of the n-alkanes increases linearly with carbon number. Therefore it is not specifically necessary to have the two nearest n-alkanes in equation 2. One of the more important advantages is the low temperature dependence. Moderate temperature differences ($<60^{o}C$) do not appreciably affect the linearity of the index, but with larger temperature differences ($>100^{o}C$) the retention index function becomes hyperbolic.

The main disadvantage is that the large volume of data tables tends to make this type of classification scheme just slightly more favorable than the trial and error method. In fact, many researchers may be forced to use the trial and error method since not all possible combinations of stationary phase and solute are recorded in the data tables. What this method does is to simply report what other chromatographers have found to be true. What is really needed is to take one step beyond this approach to where retention data can be predicted rather than just reported.

One of the more widely used and accepted classification schemes is that of Rohrschneider.[5,6] In 1959 Rohrschneider[5] first developed a polarity scale for liquid stationary phases. What he did was to measure the relative retention

time of butadiene with respect to n-butane. Butadiene, having induced dipoles at the double bonds, would be more polar than the n-butane and would therefore have a longer retention time on polar stationary phases. He then set up a polarity scale by assigning a value of 0 to a nonpolar phase (squalane) and a value of 100 to a very polar phase (ββoxydipropionitrile). The polarity of other stationary phases could then be determined from the equation:

$$P_p = a\left(\log \frac{V_p^{\text{butadiene}}}{V_p^{\text{n-butane}}} - \log \frac{V_v^{\text{butadiene}}}{V_u^{\text{n-butane}}}\right) \qquad (3)$$

where the subscripts p and u represent a polar and a nonpolar stationary phase, respectively. The term a is a normalilzation constant so that ββoxydipropionitrile will have a value of 100.

This relationship was later[6] simplified so that the new measure of polarity was the difference in the retention index between a nonpolar phase (a) and a polar phase (b).

$$\Delta I = I^b - I^a \qquad (4)$$

Both of these approaches had their disadvantages at the time. The apoproach represented by equation 3 included only polarity due to dipoles. The ability of a stationary phase to form hydrogen bonds was not specifically taken

into account. The approach represented by equation 4 represented all types of interactions in addition to simple polarity. This would make it very difficult to determine the contribution of hydrogen bonding if one had to.

In 1966 Rohrschneider[6] modified his approach to distinguish between contributions to the polarity from orientation forces, charge transfer forces, and hydrogen bonding forces. In order to do this he separated the ΔI term into 5 polarity factors (orientation, charge donor, charge acceptor, proton donor, and proton acceptor). The resulting equation

$$\Delta I = ax + by + cz + du + ev \qquad (5)$$

is a combination of the polarity factors of the solute (a,b,c,d,e) and the stationary phase (x,y,z,u,v). In order to solve this equation, 5 solutes were chromatographed on each of 5 different stationary phases. The 5 solutes that were chosen were benzene, ethanol, methylethyl ketone, nitromethane, and pyridine. Arbitrary values for x,y,z,u,v were initially chosen to be:

$$x = \frac{\Delta I_{\text{benzene}}}{100} \quad (6a) \qquad y = \frac{\Delta I_{\text{ethanol}}}{100} \quad (6b)$$

$$z = \frac{\Delta I_{\text{methylethyl ketone}}}{100} \quad (6c) \qquad u = \frac{\Delta I_{\text{nitromethane}}}{100} \quad (6d)$$

$$v = \frac{\Delta I_{\text{pyridine}}}{100} \quad (6e)$$

The calculation of all of the polarity factors includes quite a bit of work but once the a,b,c,d,e, factors are known for a particular solute its chromatographic behavior should be predictable on any given stationary phase.

Rohrschneider indices, even though they are based somewhat on arbitrary values and a largely empirical method, have been quite widely accepted even to the extent that stationary phase suppliers have taken to reporting the indices in their catalogues. It should be remembered however that this polarity index contains contributions from many different types of interactions. Therefore some experience in working with the indices may be necessary to use them properly. Problems may also occur when using the 5 polarity factors to determine the effect of orientation, charge transfer, or hydrogen bonding forces. The 5 solutes chosen by Rohrschneider have widely varying properties. Even though each one of the solutes was chosen to illustrate a specific type of interaction (i.e., ethanol-hydrogen donor) each contains some contribution from the other types of interactions. It would therefore be advisable not to rely too heavily on the 5 polarity factors unless some correction could be made to eliminate the overlap of interactions in the polarity factors.

Many researchers have used modifications of the Rohrschneider method[6] to either improve the method or to

generate Rohrschneider constants for stationary phases that Rohrschneider did not investigate. Several of these researchers[11-14] simply change the solutes that are used to determine the polarity index. Even though these attempts were made to improve the Rohrschneider method, the problem of the solutes having widely varying properties was not eliminated.

A further refinement of the Rohrschneider method was accomplished by McReynolds.[7] The retention index difference (ΔI) between the nonpolar phase squalane and over 200 other liquid stationary phases was determined for a set of 10 solutes. The 10 solutes were chosen from an original total of 68 because they were improvements over the Rohrschneider solutes with little or no loss in accuracy.

Benzene and pyridine were the only solutes to be used by both Rohrschneider and McReynolds. According to McReynolds, ethanol, methyl ethyl ketone, and nitromethane would yield retention indices of less than 500 on some stationary phases. This would prevent them from being bracketed by hydrocarbons when determining the retention indices. To avoid this problem McReynolds replaced them with the higher homologues butanol, 2-pentanone, and 1-nitropropane.

Additional solutes were added to the original 5 to improve the characterization of the stationary phases.

2-methyl-2-pentanol was added to help with branched chain compounds and 1-iodobutane was included to improve the results for halogenated compounds. It is not clear why 2-octyne, 1,4-dioxane, and cis-hydrindane were included since they only caused minor improvements and were not reported to be specific for any one type of interaction.

In his paper McReynolds wrote,[7]

> The purpose of this work is not to present a large number of liquid phases for use, but rather show the similarity of many liquid phases now in use.

When used in this manner the McReynolds constants can be helpful and the stationary phase manufactureres are correct to include them in their catalogues. However, if the McReynolds constants are to be used as a classification scheme for stationary phases, problems similar to those which occurred with the original Rohrschneider method will be encountered. The additional 5 solutes and the constants associated with them only serve to increase the complexity of classifying stationary phases.

The methods for classification of stationary phases that have been discussed to this point have been basically empirical in nature. Because of this many researchers have suggested that some method be devised that is more mathematically and theoretically rigorous. In the interest of fulfilling this need the Hildebrand solubility

treatment[15-17] has been extended for use with chromatography.[18-20]

From the classical solubility parameter approach of Hildebrqnd[15-17] the solubility parameter (δ) of a compound can be defined as the square root of the cohesive energy density

$$\delta = \left(\frac{\Delta E^V}{V}\right)^{\frac{1}{2}} \qquad (7)$$

where E^V is the energy of vaporization of the pure compound at 25°C, and V is the volume of the solution. Unfortunately Hildebrand's treatment only took into account nonpolar compounds.

Later Blanks and Prausnitz[21] and Gordon[22] extended the solubility parameter to include polar systems. In order to do this they assumed that the intraction energies in solution (E) could be expressed as the sum of the contributions of the dispersion and polarity interactions. This was further expanded by Hansen[23] to also include hydrogen bonding.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2 \qquad (8)$$

Keller et al.[18] further postulated that the polar contribution was a combination of orientation (δ_o), induction (δ_i), as well as dispersion interactions and the hydrogen bonding

interaction was a combination of proton acceptor (δ_a) and donor (δ_b) interactions.

$$\delta^2 = \frac{E^v}{V} = \delta_d^2 + \delta_o^2 + 2\delta_i \delta_d + 2\delta_a \delta_b \qquad (9)$$

Where dispersion interactions are calculated from refractive index data, orientation interactions from the dipole moment, and induction interactions from the polarizability. Proton donor and acceptor interactions may be estimated from δ values for compounds with both donor and acceptor functional groups, or from corresponding spectral, calorimetric, or gas chromatographic data. In most cases the calculation of δ is simplified by a cancellation of terms.

What we have in this extended solubility parameter which has been expanded for use with polar compounds is precisely what we have been looking for. Each of the major types of interaction has been defined so that it can be separated from the general definition of polarity. The resulting table of δ_d, δ_o, δ_a, δ_b, δ_i, values for stationary phases would not have the overlap of interactions that other classification schemes have, thus making it much easier to interpret. Unfortunately such tables are only available for common solvents not stationary phases. Perhaps it is the complexity of the structures of the stationary phases that makes these calculations difficult if not impossible to solve.

Along with the chromatographic approaches that have been discussed in this chapter, several researchers[24-27] have used relative retention times for their measurements of stationary phase polarity. These methods require that a combination of 2 solutes, called a probe pair, be chromatographed on a stationary phase and the relative retention time between the two solutes be calculated. The relative retention time can then be used as the measure of polarity or any other type of interaction that the probe pair is specific for.

Burns and Hawkes[27] developed a method for classifying stationary phases based on the logarithm of the relative retention time of a probe pair. Their classification scheme included parameters for dispersion, polarity, acidity, and basicity. The dispersion interction was calculated from the refractive index of the stationary phase as was previously mentioned in this chapter.

Benzene and n-heptane were chosen as the probe pair for the polarity parameter. The aromaticity of the benzene ring causes an induced dipole so that on a polar phase it would be held more strongly than the n-heptane. The acid-base effects of this probe pair would not cause any significant problem, but the different dispersion potentials are a problem and had to be corrected for. Their polarity index could then be calculated by the equation:

$$P = 10 \log \left(\frac{t_{benzene}}{t_{n\text{-}heptane}} \right) 6.4 - \left(\delta_d{}^x - 4.7 x \delta_d \right) \frac{590}{2.3RT} \qquad (10)$$

The basicity index was calculated from the relative retention time of butanol with respect to ethyl acrylate. Only a small correction was needed since the relative retention time was not unity on any stationary phase.

$$B = 10 \left[0.1 + \log \left(\frac{t_{butanol}}{t_{ethyl\ acrylate}} \right) \right] \qquad (11)$$

The least reliable index was the acidity. Burns and Hawkes relied on published data and this led to their using pyridine and benzene as their probe pair for acidity. Benzene adequately compensates for the dispersion interaction of the pyridine. However, the large dipole of pyridine cannot be compensated for in the dipole-dipole and dipole-induced dipole interactions between pyridine and the stationary phase. The dipole-dipole interaction was compensated for by using the polarity index (P) from equation 10 and an empirical constant. The dipole-induced dipole interaction was completely ignored. It was suggested that the acidity index (A) be used only qualitatively.

$$A = 5 \left[\log \left(\frac{t_{pyridine}}{t_{benzene}} \right) \frac{P}{22} - 0.13 \right] \qquad (12)$$

The work of Burns and Hawkes[27] made an attempt to calculate the individual interactions of stationary phases. Unfortunately because of their reliance on published data, mathematical corrections which were based according to the authors on inadequate theoretical foundation, were necessary. In addition some of the indices were obtained by dubious analogies. The major problem with the work of Burns and Hawkes was the reliance on published data and the lack of experimental work. The solution of this problem for the case of acidity and basicity indices will be attempted in this present work.

The approach that will be used can be shown to follow from the extended solubility parameter of Keller et al.[18] The solubility parameter (δ) can be expressed for each of the solutes in the probe pair as:

$$\delta_1^2 = \frac{E_1^v}{V_1} = \delta_{d_1}^2 + \delta_{o_1}^2 + 2\delta_{i_1}\delta_{d_1} + 2\delta_{a_1}\delta_{b_1} \qquad (13)$$

$$\delta_2^2 = \frac{E_2^v}{V_2} = \delta_{d_2}^2 + \delta_{o_2}^2 + 2\delta_{i_2}\delta_{d_2} + 2\delta_{a_2}\delta_{b_2} \qquad (14)$$

subtracting equation 14 from equation 13 yields:

$$\delta^2 = \Delta\left(\frac{E^v}{V}\right) = (\delta_{d_1}^2 - \delta_{d_2}^2) + (\delta_{o_1}^2 - \delta_{o_2}^2) + 2(\delta_{i_1}\delta_{d_1} - \delta_{i_2}\delta_{d_2}) + 2(\delta_{a_1}\delta_{b_1} - \delta_{a_2}\delta_{b_2}) \qquad (15)$$

If a probe pair is chosen such that the interactions due to dispersion (δ_d), induction (δ_i), and dipole (δ_o) are identical, equation 15 can be simplified to:

$$\delta^2 = \Delta\left(\frac{E^V}{V}\right) = 2(\delta_{a_1}\delta_{b_1} - \delta_{a_2}\delta_{b_2}) \qquad (16)$$

If the acidities of the probes are also identical, the resulting solubility parameter would be solely a function of the basicity of the probes. The relative retention time could then be used as a measure of the acidity of the stationary phase without any corrections. A similar argument could be made for the basicity of a stationary phase.

In this approach the choice of the probe pair is critical. In order to eliminate the contribution of the other interactions the properties of the probe pair must be carefully matched so that they differ only in the proper interaction. For example if we want to measure the acidity of a phase we must find a pair of solutes that have similar polarities and dispersion interactions, no acidity, and quite different basicities. By matching the properties in this way the only interaction that will cause any separation of the solutes is the formation of a hydrogen bond between the stationary phase (acid, proton donor) and the solute (base, proton acceptor) molecules. The stronger

base of the probe pair will be held longer on the acidic stationary phase because of the formation of a hydrogen bond. Therefore, the greater the relative retention time becomes, the more strongly acidic the stationary phase. Similar arguments can be made for polarity, dispersion and basicity measurements.

In order to choose the proper solutes for acidity and basicity measurements, Kirkland's[28] table of extended solubilities was consulted.

This approach gives us precisely what we have been looking for. The experimental technique is relatively easy to use, requiring only one probe pair for each type of interaction. It is also very specific since each type of interaction can be completely separated from the other types of interaction. Most of all this type of classification scheme would be uncomplicated to use. Little or no previous experience with chromatography and stationary phases, and only a small amount of chemical intuition would be required to use this method.

To work at its best the chromatographer should know something about the functional groups on the sample molecules that are to be separated. By knowing what types of interactions would attract one of the sample molecules more than the other components of the sample, a proper stationary phase could be chosen. The only problem that

would occur would be when nothing was known about the sample. However in this case, this type of classification scheme would provide an excellent starting place for trial and error methods. One could logically approach the problem by starting with four stationary phases which strongly exhibit the major types of interaction (dispersion, polarity, acidity, basicity) then branch off to combinations of the interactions which show the most promise. At any rate, this approach appears to be a major improvement over previous attempts at a liquid stationary phase classification scheme.

Specifically what this thesis is attempting to accomplish is to generate acidity and basicity parameters for the silicone based stationary phases on the Hawkes committee's list[29] of preferred stationary phases.

CHAPTER 3

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC APPROACH

Introduction

In addition to the chromatographic approach to acidity and basicity measurements, many researchers have reported success with spectrophotometric methods. A majority of these methods require that a 1:1 complex be formed before any measurements can be made. These complexes are held together by the formation of hydrogen bonds between the proton donating acid and the proton accepting base. Normally one of the components of the 1:1 complex is not changed while many compounds are complexed to it. Most spectrophotometric methods will measure the change in position or intensity of an absorption peak which has been created by the formation of a hydrogen bond. Results, in the form of equilibrium constants, can then be obtained from these spectrophotometric measurements. Conclusions, as to acid or base strength, can then be drawn by comparing the equilibrium constants for the formation of various complexes.

Historical

The first spectroscopic detection of hydrogen bonds was

accomplished around 1930 by the use of infrared spectroscopy.[30] Primary interst was awarded to the A←H···B symmetric stretch (ν_s=3500-2500 cm^{-1}).[31] This stretching mode (ν_s) was fround to be particularly sensitive to the formation of hydrogen bonds.

The formation of a hydrogen bond will have an effect on the position, shape, and size of the ν_s absorption peak. When a hydrogen bond is formed the frequency of ν_s is shifted to lower frequencies. Badger and Bauer[32] were among the first to attempt to correlate this frequency shift with the energy of the hydrogen bond. Their methods were questioned by some but the conclusion that the energy of the hydrogen bond is proportional to the ν_s frequency shift was not. In addition to the frequency shift, the band width of ν_s also changes upon formation of a hydrogen bond. The characteristic broadening of ν_s when a hydrogen bond is formed has been found to be linearly proportional to the frequency shift.[33,34] Through this relationship with ν_s, the bandwidth could be related to the strength of the hydrogen bond. The most sensitive property that can be used to determine hydrogen bond strength is the band intensity. The integrated absorption of ν_s increases greatly upon hydrogen bond formation.[34,35] Since the band intensity is so sensitive to hydrogen bond formation it is a better method than either frequency shift or

bandwidth measurements. However, because of the extreme sensitivity to temperature changes and the inconsistencies between researchers over the range for the integration, the band intensity measurements are not completely reliable.

In the early 1940's the formation of a hydrogen bond was found to have an effect on the electronic absorption spectra in the UV-VIS region. One of the first researchers in this area was Durunikhin[36] who observed a color change in dyes due to hydrogen bonding. The observed color change corresponded to a shift in frequency of the UV-VIS absorption peak. Most of the early work on hydrogen bond detection by UV-VIS spectroscopy was accomplished by dye chemists. However, when the UV-VIS technique began to show promise, the theoretical chemists took over the initiative. Their main interests seemed to be with assigning transitions for the frequency shifts and interpreting the red and blue shifts.

In 1949 Benesi and Hildebrand[37] took a more practical approach to the study of hydrogen bonding by UV-VIS spectroscopy. In their work they developed an expression for the equilibrium constant for complex formation between iodine and several aromatic hydrocarbons. The method requires that a 1:1 complex be formed. Equilibrium constants can then be calculated from the difference in peak

intensities between the complex and the free solvent. There have been many slight modifications[38-41] but for the most part the method remains one of the best equilibrium constant calculations for weak complex formation. One of the most important modifications of the Benesi-Hildebrand (BH) equation was brought about by the introduction of high resolution nuclear magnetic resonance spectroscopy (NMR).

In 1951 Arnold and Packard[42] observed a change in the NMR chemical shift for the -OH proton of ethanol as the temperature was increased. This was attributed to the dissociation of hydrogen bonds by both Arnold and Packard[42] and Liddel and Ramsey.[43] Further study revealed that NMR measurements were extremely sensitive to the formation of hydrogen bonds. The resonance position of the hydrogen bonding proton was found to be dependent on both temperature and dilution. The increased sensitivity of NMR measurements made it possible to detect weak hydrogen bonds that could not be detected by IR frequency shift measurements. The only technique that could match the NMR methods would be the IR intensity measurements. However, because of the previously stated problems with the IR band intensity measurements and their related unreliability, NMR is the more favorable method for the detection of weak hydrogen bonds. IR and NMR methods tend to compare

quite favorably when strong hydrogen bonds are under observation.

Theory

The thing that makes NMR extremely useful is the ability to identify chemically different nuclei of the same isotopic species. Knight[44] was one of the first to observe that the characteristic resonance frequency of a particular nucleus was dependent on its chemical environment. A separate absorption signal can then be observed for each type of chemically different nucleus. This is known as the chemical shift.

Chemical shifts are brought about because the magnetic field that the nucleus experiences is determined by its environment. The major constituent of the nuclei's environment will consist of shielding or screening of the magnetic field by the nearby electrons. Nuclei which are heavily shielded by electrons will require higher magnetic field strengths to cause an absorption than the more lightly shielded nuclei. These slight differences are what lead to the high resolution NMR spectrum.

Chemical shifts in the NMR spectrum are measured in parts per million (ppm) of the applied magnetic field (60 Hz in 60 MHz). For proton NMR tetramethylsilane (TMS) is the most popular reference material. All of the protons

in TMS are chemically equivalent and highly shielded so that the spectrum will contain a single resonance peak located at high magnetic field strength. This resonance peak is assigned a value of 0.0 on the δ scale. Most of the protons in organic compounds will have resonance peaks between 0.0 and 10.0 δ with 1 δ unit equal to 1 ppm. δ values near ten are said to be downfield and are associated with low magnetic field strengths and little shielding by the electrons. δ values near zero are said to be upfield and are associated with high magnetic field strengths and a great deal of screening by the electrons.

In addition to shielding by electrons there can be many other contributions to the chemical shift. Such things as anisotropy, solvent effects, self association, complex formation, and hydrogen bond formation can play an important part in determining the position of a resonance peak.

Systems which have NMR spectra that are independent of their orientation to the applied magnetic field are termed isotropic. These systems would include gases, low viscosity solutions, and molecules which possess spherical symmetry. Unfortunately, the systems that are being studied here do not fit into the isotropic category. The NMR spectra for the liquid stationary phases would depend on the orientation of the stationary phase to the

applied magnetic field. Systems which exhibit this dependence are defined as anisotropic.

When a molecule, which does not possess a great deal of symmetry, is placed in an external magnetic field (H_o) a secondary magnetic field will be induced in a portion of that molecule. The magnitude of this secondary magnetic field will be much less than H_o but it will still have an effect on the shielding experienced by the nearby nuclei. The effect of anisotropy on the NMR spectrum will then be to shift the position of one or more of the resonance peaks. The direction of the shift can be either upfield or downfield depending on whether the anisotropy leads to more or less shielding of the nuclei.

Solvent effects come in many forms and play an important role in determining the environment around a nucleus. The total effect on the chemical shift can be summarized as follows[45]

$$\sigma_{solvent} = \sigma_B + \sigma_W + \sigma_A + \sigma_E$$

σ_B is the contribution to the total solvent effect due to the bulk magnetic susceptibility of the medium. This can be almost completely compensated for by the use of an internal reference. Since TMS will be used as an internal reference for all measurements the bulk susceptibility of the medium can be ignored.

The effect of the formation of weak Van der Waals forces (σ_W) between the solute and solvent can also alter the environment of a nucleus. Shifts on the order of 0.1-0.2 ppm have been observed[45] where the Van der Waals interaction was considered to be the dominant effect. However, because of the choice of experimental conditions, any shifts due to Van der Waals interactions should cancel out and not be a factor in the final calculations.

σ_A results from the anisotropy of the solvent molecule. Highly anisotropic molecules containing aromatic rings, C=O, C=C, C≡C, or C≡N, can have a large effect on the chemical shift of the nucleus. The influence of a secondary magnetic field caused by an anisotropic group in the solvent molecule can lead to either increased or decreased shielding of a nucleus. In this experiment 1,1,1,trichloroethane and chlorobenzene will be used as solvents. These molecules will cause some anisotropic effects but because of the experimental methods that will be used any effect will be cancelled out. The ideal solvent for this work is carbon tetrachloride which is a symmetrical molecule and would not have any anisotropic effects. Unfortunately, the liquid stationary phases that were used for this study were not soluble in carbon tetrachloride.

σ_E refers to the effect due to a polar solvent molecule. The polar group of the solvent molecule will generate

an electric field which when directed towards a nucleus will greatly effect its environment. Depending on which end of the dipole is oriented towards the nucleus, shielding can either be increased or decreased. Normally the effect is to reduce the amount of shielding around protons, thus causing downfield shifts. However, as has been the case for other of the solvent effects, the polar effects will cancel out and not be a factor because of the choice of experimental conditions which will be explained in detail in chapter 5.

In addition to the solvent effects it is also possible to alter the chemical shift of a resonance peak through the formation of a complex. These complexes normally are formed by intra or intermolecular self association or hydrogen bonding. Since this work will be accomplished purely with proton NMR, all following discussions will assume that protons are the nuclei under study.

When protons are involved the most common way for a complex to be formed is through the formation of a hydrogen bond. Pimentel and McClellan[31] defined hydrogen bonding as follows: A hydrogen bond exists between a functional group (A-H) and an atom or group of atoms (B) in the same or different molecule when:

a) There is evidence of bond formation (association or chelation)

b) There is evidence that this new bond linking A-H and B specifically involves the H atom already bonded to A.

Protons which are bonded to carbon atoms usually do not take part in hydrogen bonds. The most common source of protons for hydrogen bond formation are alcohols, carboxylic acids, and amines. Hydrogen bonds can also be formed between the proton and the π electrons in an aromatic ring, but this type of hydrogen bond is not as common.

Intramolecular self association can occur between different parts of the same molecule. The requirements are that there be a proton donating group close enough to a proton accepting group in the same molecule so that a hydrogen bond may be formed. In most cases this is possible only in large molecules or polymers. There is no way intramolecular self associastion can be eliminated or compensated for. The only hope is that either the amount of intramolecular self association is very small or the self associating species has a greater affinity for the species that you want it to complex to than it does for itself.

A more common problem is intermolecular self association. Here one molecule will complex with another identical molecule. This commonly occurs to a large extent with alcohols and acids. Dimers need not be the only type

of complexes that can form, trimers and even tetramers have been observed.[46] This type of self association can cause problems, including shifting the position of the hydrogen bonding protons resonance peak several ppm in concentrated solutions. The only way that this can be compensated for is to work with very low concentrations of the self associating species. At these very low concentrations (<0.01 M) the effect of self association will be greatly overshadowed by the formation of other hydrogen bonds with the sample.

The most important type of complex formation from the standpoint of this study is the formation of hydrogen bonds between different molecules. The strength of this type of hydrogen bond is proportional to the shift of the resonance position of the hydrogen bonded proton. Exactly how the strength of the hydrogen bond is to be determined will be discussed at a later time.

For any hydrogen bonding or self associating system the participating molecules will be in equilibrium between their associated and nonassociated states.

$$A\text{-}H + B \rightleftharpoons A\text{-}H\cdots B \qquad (17)$$

The observed NMR spectrum for this system will then be dependent on the rate of exchange between the associated and nonassociated states. If there is no exchange taking place it is obvious that separate signals will be observed

for AH and B. Separate signals will also be observed if the rate of exchange between the two states is very slow. In order for these separate signals to be observed the lifetime of each state must be greater than the reciprocal of the shift (in frequency units) due to the formation of the hydrogen bond. In the case of NMR measurements this time is on the order of 10^{-2} to 10^{-3} seconds. However, most hydrogen bonding systems have exchange rates much faster than 10^{-3} seconds. What will then be observed in these systems is a single resonance peak for the hydrogen bonding proton that represents a weighted average between the associated and nonassociated positions of the proton.

For hydrogen bonding systems the position of this weighted average resonance peak will be located downfield from the nonassociated position. The reason for this downfield shift has not been fully explained. In order for this downfield shift to occur the hydrogen bonded proton must be deshielded, but this is not thought to be simply a matter of decreased electron density around the proton. When the hydrogen bond is formed, the proton is probably in an area of increased electron density when compared to the nonassociated state. However, the electron distribution in the A-H bond is apparently altered by the presence of B in such a way that the proton is deshielded. In essence the molecule B probably has a

neighbor anisotropic effect on the proton, where an induced magnetic field in B alters the electron distribution around the proton in such a way that the proton is deshielded.

Now that we know that upon formation of a hydrogen bond we will observe an averaged resonance peak which has been shifted to lower magnetic field strength, the question arises as to how we can determine the strength of the hydrogen bond from the magnitude of the shift that it causes. To answer this question we must go back to the work of Benesi and Hildebrand.[37]

The equation that was derived by Benesi and Hildebrand[37] related the molar absorptivity coefficient of the complex (ε_c) with the equilibrium constant for complex formation between iodine and an aromatic hydrocarbon.

$$\frac{[I_2]\,\ell}{\log I_{o/I}} = \left(\frac{1}{K\varepsilon_c}\right)\left(\frac{1}{[A]}\right) + \frac{1}{\varepsilon_c} \qquad (18)$$

where

$$\varepsilon_c = \frac{\log I_{o/I}}{[c]\,\ell} \qquad (19)$$

Where [A] & [C] are the concentrations of the aromatic hydrocarbon and complex respectively, I & I_o are the

intensities at the wavelength of maximum absorption and ℓ is the cell path length.

In the following years there were many modifications made on the Benesi-Hildebrand (B-H) equation.[38-41,47-49] The one thing that all of the methods had in common was the linearity of the plots that were used for the calculation of the equilibrium constants.

In 1963 Mathur et al.[50] modified the B-H equation to use NMR frequency shifts. Their final equation closely resembled that of Baba and Suzuki[41] with the exception of the substituition of NMR frequency shifts for the molar extinction coefficients that were used for the UV-VIS methods. Mathur et al.[50] derived their equation in the following manner.

First it should be noted that the following derivation only takes into account a 1:1 complex where one proton donating molecule hydrogen bonds to one proton accepting molecule. This assumption can be made because of experimental precautions against 2:1, 3:1, or higher order complexes being formed. These experimental details will be explained in greater detail in chapter 4.

For the equilibrium reaction

$$AX + B \rightleftharpoons A\text{-}X\cdots B \qquad (17)$$

the equilibrium constant can be expressed as

$$K = \frac{[AX\cdots B]}{[A][B]} = \frac{[C]}{[A][B]} \qquad (20)$$

where C denotes the complex, A is the acid or proton donor, and B is the base or proton acceptor. Since we are using an NMR method it is impossible for us to measure the equilibrium concentrations of the complex (C) or the base (B). The equilibrium constant can however be expressed in terms of the original concentrations of acid (A_o) and base (B_o) as well as the concentration of free acid (F) which remains at equilibrium.

$$K = \frac{[C]}{[A][B]} = \frac{A_o - F}{F(B_o - A_o + F)} \qquad (21)$$

As was stated earlier reaction 17 proceeds very rapidly. The observed hydrogen bonding resonance peak will then be a weighted average of the position of the free and complexed proton resonance peaks.

$$\delta_{obs} = \left(\frac{F}{A_o}\right)\delta_f + \left(\frac{A_o - F}{A_o}\right)\delta_c \qquad (22)$$

Where δ_{obs} is the observed chemical shift in ppm on the δ scale and δ_f & δ_c are the chemical shifts of the free and complexed proton resonance peaks. Equation 22 can then be rearranged to

$$\delta_{obs} = \delta_f + \left(\frac{A_o - F}{A_o}\right)\Delta_c \tag{23}$$

where

$$\Delta_c = \delta_c - \delta_f \tag{24}$$

Rearranging equation 21 and substituting into equation 23 yields

$$\delta_{obs} - \delta_f = \frac{FK(B_o - A_o + F)}{A_o}\Delta_c \tag{25}$$

Now we must make the assumption, and arrange experimental conditions in such a way that $B \gg A$ and $B \gg A-F$. Using these assumptions equation 21 becomes

$$K = \frac{A_o - F}{FB_o} \tag{26}$$

Using this new expression for the equilibrium constant, equation 26 can be combined with equation 23 to yield

$$\delta_{obs} - \delta_f = \frac{KFB_o\Delta_c}{A_o} = \frac{KB_o\Delta_c}{KB_o + 1} \tag{27}$$

Rearrangement of equation 27 will give us a modified version of the B-H equation that can be used with NMR measurements.

$$\frac{1}{\delta_{obs} - \delta_f} = \left(\frac{1}{K\Delta_c}\right)\left(\frac{1}{B}\right) + \frac{1}{\Delta_c} \tag{28}$$

It can now be seen that equation 28 is of the form $y = mx+b$. A plot of $1/\delta_{obs}-\delta_f$ vs $1/B$ should yield a straight line. The intercept of the line will be $1/\Delta_c$ and the equilibrium constant can be calculated from intercept/slope. Wong and Ng[51] further modified equation 28 to a simpler form.

$$\frac{1}{\delta_{obs}} = \frac{1}{\delta_c} + \left(\frac{1}{[B_o]}\right)\left(\frac{1}{K\,\delta_c}\right) \qquad (29)$$

Although it appears that the B-H equation is a simple straightforward method for calculating equilibrium constants, many researchers have observed nonlinearities in the plot and have developed modifications to correct the problems.

Self association, especially of the acid, can cause major problems. Since the strength of a hydrogen bond that is formed with the stationary phase will be much weaker than the self association hydrogen bond, it may not be favorable for the bond to the stationary phase to be formed. This would result in NMR measurements on the amount of self association not on the desired hydrogen bond with the stationary phase. To correct this problem, Wong and Ng[51] observed that the base concentration must be about 20 times greater than the acid concentration. This also corresponds to the assumption that was made for equation 26 in the derivation of the modified B-H equation. Wong and Ng[51] also determined

that the concentration of the base had to be low enough so that the dielectric constant of the solution would not be significantly changed. They recommended a maximum base concentration of about 2 M which would correspond to an acid concentration of about 0.05 M. To insure reliability they suggested that NMR measurements be taken over a 3 fold change in base concentrations.

Some researchers[52-56] have suggested that some solvents may act as a proton acceptor or donor. Chloroform was found to be a particularly poor choice because of its weakly acidic nature. Dixon[55] suggested that CCl_4 was a weak proton acceptor and would be unacceptable as a solvent. However, Gramstad and Becker[57] could find no evidence of a hydrogen bonding complex between CCl_4 and phenol. Further study by Christian and Tucker[58] found that chemical shifts for hydrogen bonded complexes in CCl_4 were neither superior nor inferior thermodynamically when compared with corresponding measurements in hydrocarbon solvents. Since 1,1,1, trichloroethane is chemically similar to CCl_4, it can be assumed that it would not interfere with the basicity measurements. On the other hand because of the aromatic ring, chlorobenzene might act as a weak proton acceptor in the acidity measurements. This problem will be discussed in chapter 5.

Nonlinearities have been observed in the B-H plot

depending on the concentration units that are used.[39] Johnson et al.[59] have resolved these problems. They found that an improper choice of concentration units could cause large errors. Mole fraction and molarity units have been shown to be poor choices for the concentration units. Their observations pointed to molarity as the proper choice for the concentration units to describe the average properties of 1:1 complexes.

What we have now is a method for the calculation of equilibrium constants for weak hydrogen bonded 1:1 complexes. The question now arises as to how the equilibrium constants will be used to determine the acid or base strength of the liquid stationary phases.

The base strength will be determined with the help of the acid chloroform. 1:1 complexes will be formed between chloroform and each of the stationary phases. For each of the complexes the chloroform concentration will be held constant at 0.1 M and the stationary phase (base) concentration will be varied from 2.0 M up to about 2.5M.

For acid strength quinuclidine will be used as the base for each complex. The quinuclidine concentration willl be varied from 2.0 M to about 0.5 M while the stationary phase (acid) concentration will be held at a constant 0.1 M.

In each case the equilibrium constant itself will be the measure of acid or base strength. The larger the equilibrium constant the stronger the complex which has formed and therefore the more acidic or basic the stationary phase.

CHAPTER 4

EXPERIMENTAL WORK

Gas Chromatography

Instrumentation

A Perkin Elmer model 3920 gas chromatograph was used for all of the gas chromatographic work. The chromatograph is equipped to handle either one or two columns. The oven is thermostatted in such a way that the temperature will not vary more than 1% in the temperature range from ambient to 399°C. The injector port can be heated to ensure proper volatilization of samples to prevent tailing of peaks. The interface between the end of the column and the detector can also be heated to guard against condensation. The injector and interface temperature was approxiomately 50°C higher than the column temperature.

This chromatograph possesses two flame ionization detectors (one for each column). The flame ionization detector uses an air/hydrogen flame to ionize the sample molecules as they elute from the column. The electrons which result from this ionization are then collected by an electrode which is located just above the flame. This ionization current is applied to an electrometer

amplifier and is then available for the input to a strip chart recorder.

Helium was used as the carrier gas. Because of the air/hydrogen flame it was not possible to use air to obtain the unretained time (t_m). For this reason methane was used instead of air with a negligible difference. All of the samples were injected with a 2.5 µl Hamilton hypodermic syringe with the exception of the methane which was injected with a gas tight 100 µl Hamilton hypodermic syringe.

Choice of Solid Support

The major interest of this work was to investigate the acid-base interactions between stationary phase and probe pair molecules. For this reason it was necessary to select a solid support that would not interfere or add to the interactions under observation. Adsorption of the solute onto the solid support would tend to distort the retention pattern as well as alter the relative retention times from those that would normally be predicted. A solid support that would not cause these problems would be glass beads.

Glass beads would cause little adsorption mainly due to their low surface area. As the size of the glass beads is decreased the spaces between the beads

becomes smaller which leads to less zone dispersion. However, if the size of the beads gets too small very high pressures would be necessary to force the mobile phase through the column. In addition, very small beads would have a larger surface area to column volume ratio which would add to the probability of adsorption. Since the main need of this work is to minimize adsorption rather than maximize efficiency, larger glass bead size can be tolerated. It was decided that 60-80 mesh glass beads would provide adequate resolution with only a small amount of zone dispersion and very little adsorption.

Choice of Stationary Phases

The silicone base stationary phases from the Hawkes committee's[29] list of preferred stationary phases were chosen as the phases to work with. Supelco stationary phases were donated for this study by Walter Supina of Supelco Inc. The stationary phases included: dimethylsilicone (SP-2100), phenylmethylsilicone (SP-2250, 50% phenyl), methylcyanopropopylsiloxane (SP-2300, 36% cyanopropyl; SP-2310, 55% cyanopropyl; SP-2330, 68% cyanopropyl; SP-2340, 75% cyanopropyl), trifluoropropylmethylsiloxane (SP-2401), and 2-4% aminoalkymethylsiloxane from Petrarch Systems Inc.

Column Construction

In making the decision about the type of material to use for the column several requirements were considered:[60] The column should not catalytically decompose the sample, it should not absorb the sample, it should be capable of being packed with an efficient packing structure, it should be easily installed. The best material that fit these criteria was stainless steel. The columns were constructed with ¼" o.d. stainless steel tubing which was cut into 8 ft. lengths. In order to clean the inside of the tubing of oil, grease, and metal fragments, each column was rinsed with the following solutions in the following order: chloroform, methanol, distilled water, 6 M nitric acid, distilled water, and methanol.

The volume of the column was then calculated. Using the density of the glass beads (2.98 g/ml), and the assumption that only 62% of the total volume would be occupied by the glass beads, the weight of the glass beads that was necessary to fill the column was calculated. Because of the small surface area of the glass beads the amount of stationary phase was restricted to 0.5% of the weight of the glass beads.

The packing procedure was the same as that suggested by Supina.[61] The proper amount of stationary phase was first dissolved in a solvent. The solvent-stationary

phase solution was then mixed with the proper weight of glass beads. The solvent was then evaporated off by gentle heating. The mixture was stirred constantly during this procedure to ensure an even coating of the glass beads by the stationary phase. The coated glass beads were then placed into the column. To ensure a tight efficient packing, a combination of bouncing and vibration was used. Once the packing was complete the tubing was coiled so that it would fit in the oven of the chromatograph.

Choice of Probe Pairs

Since both acidity and basicity measurements were made it was necessary to find a probe pair for each. As was stated previously in chapter 2 most of the interactions that the solutes are capable of must be either identical or nearly so.

For acidity measurements a set of solutes must be found that have nearly identical dispersion and polarity interactions, no acidity, and quite different basicities. Such a probe pair was found to be propylamine and propylchloride which have the following properties:

	δ_D	δ_O	δ_B	δ_A
propylchloride	7.3	3	0	0
propylamine	7.3	4	6.5	0.5

Being unable to obtain both compounds from chemical stores the higher homologues butylchloride and butylamine were used as the acidity probes instead. It was assumed that the properties would be very similar to the lower homologues.

By an argument similar to that for acidity measurements the basicity probes should have nearly identical dispersion, polarity, and basicity indices with widely varying acidities. By consulting the published tables of Kirkland[28] the best choice for the basicity probes appeared to be ethanol and acetone:

	δ_D	δ_O	δ_B	δ_A
ethanol	6.8	4	5	5
acetone	6.8	5	2.5	0

The only real problem with this choice is the different basicity indices. This difference might lead to some unreliability in the basicity measurements.

Procedure

Before any of the columns could be used they had to be conditioned. This can be accomplished by heating the column to a temperature that is higher than any temperature that might be used during the analysis while passing helium through it. This is best done in the chromatograph oven but to avoid contamination the end of the column should

not be attached to the detector. The columns were conditioned at 175°C for approximately three hours. All chromatographic measurements were made at 75°C.

In order to assure that the columns were operating properly a mixture of a homologous series of n-alkanes was run through each of the columns. Methane was used to obtain the unretained time. The retention time from the methane peak for each of the hydrocarbons was then measured. For a properly operating column, a plot of the logarithms of the retention times of the hydrocarbons vs. the number of carbon atoms should yield a straight line. If a straight line is not obtained something is wrong with the column and it may need to be repacked.

Methane and each of the four probe pair solutes were injected onto each of the columns. Because of the difficulty of injecting methane with liquid samples and the lack of resolution between ethanol-acetone and butylchloride-butylamine mixtures, each compound was injected separately. Several injections were made for each compound on each column to average out any slight differences in injection technique. On each column the retention time from injection for methane was subtracted from the retention time from injection for each of the probes to obtain the sorbed time which was used for the relative retention time calculations.

Nuclear Magnetic Resonance Spectroscopy

Instrumentation

A Varian EM-360 60 MHz nuclear magnetic resonance spectrometer was used for all measurements. Larger more powerful instruments are available but due to cost limitations and the large amount of time that was necessary to obtain spectra for the numerous samples, it was not practical to use the other instruments. The 60 MHz instrument provided adequate resolution for the measurements that were made. Sample cells of eggshell glass were used and spun in the sample cell to average out any inhomogeneities in the glass. All measurements were made at the temperature of the magnet which was room temperature.

Choice of Solvent

The ideal solvent for proton NMR work is one that doesn't have any protons. By not having any protons the solvent would be invisible to the proton NMR spectrometer. For this reason carbon tetrachloride (CCl_4) was chosen as the solvent. Unfortunately the stationary phases which are being used are not completely soluble in CCl_4. Other solvents had to be found which would not have any acidity or basicity that would interfere with the formation of the hydrogen bond between the stationary phase and either the acid or

the base. Another important factor in this selection is that the position of the proton resonance peaks from the solvent cannot interfere with the position of the resonance peak for the hydrogen bonded proton. In the case of the basicity measurements 1,1,1, trichloroethane was determined to be a good solvent. For the acidity measurements chlorobenzene was chosen as the solvent. It was assumed that any acidity or basicity of these solvents was negligible when compared to that of the other components in the solution. Possible problems with anisotropy and solvent effects will be discussed in more detail in chapter 5.

Choice of Acid and Base

When making basicity measurements on a stationary phase a hydrogen bond must be formed between the stationary phase and a suitable proton donating acid. It was discovered that weaker acids would work better because strong acids such as phenol might become completely deprotonated by the more stronlgy basic stationary phases. This would place the acidic proton in an environment other than the 1:1 acid-base complex that is desired. For this reason the acid that was found to work the best was chloroform.

In a similar way the acidity measurements require that a hydrogen bond be formed between the stationary phase and a suitable proton accepting base. The choice of quinuclidine

as the base was made primarily on the work of Slejko and Drago.[62] They chose quinuclidine as the base for their work because of its low anisotropy and its fairly strong basicity. Their paper was one of the only ones to investigate the acidity of various compounds. Most other researchers were investigating only basicity.

Procedure

The procedure for both acidity and basicity measurements is basically identical. The only difference is that for acidity measurements the stationary phase is the acid and quinuclidine is the base and for basicity measurements the stationary phase is the base and chloroform is the acid.

Solutions must be prepared with a constant concentration of the acid and varying concentrations of the base. For all measurements the concentration of the acid was held constant at 0.1 M. For acidity measurements the quinuclidine concentration was 0.5 M, 1.0 M, 1.5 M, 2.0 M, and 2.5 M. For basicity measurements the stationary phase concentration was 2.0 M, 2.15 M, 2.25 M, 2.35 M, and 2.5 M. The only exception was the 2-4% aminoalkymethylsiloxane whose concentration was 1.4 M, 1.5 M, 1.6 M, 1.7 M, and 1.8 M. These lower concentrations were necessary because the density was low enough so that a 2 M solution would exceed the capacity of a 5 ml volumetric flask.

It was assumed that these concentrations were high

enough to eliminate any self association of the chloroform. The concentration range of the stationary phases was not the 3 fold range suggested by Wong and Ng[51] for good reliability but there was not enough of the donated stationary phases and not enough money was available to buy more.

The solutions were prepared by weighing the proper amount of the acid and base, adding a couple of drops of TMS, and diluting to the mark with the proper solvent. Since all of the stationary phases were polymers the molecular weights that were necessary to calculate the molarities were based on the repeating group of the polymer. In the case of the cyanopropyl stationary phases the percentage of the cyanopropyl group was taken into account so that a 2 M solution would contain 2 moles of the cyanopropyl group. In the case of the 2-4% aminoalkymethylsiloxane it was impossible to know the structure of the repeating group. Molarities were based on the molecular weight of the amino group and the assumption that on the average 3% of the stationary phase contained that amino group.

Following preparation, the NMR spectrum of each solution was taken. The identification of the hydrogen bonded proton's resonance peak was simplified by the fact that it was the only peak that shifted its position as the concentration of the base was increased. All NMR measurements were made in the δ scale (ppm) using TMS as the reference peak (0.0 ppm). Calculations were then accomplished by the method

described in chapter 3 using equation 29.

Statistics

After measuring the chemical shift of the hydrogen bonded proton for each solution a linear regression analysis for each stationary phase was run. This analysis provided the slope, intercept, and correlation coefficient for each plot of $1/\delta_{obs}$ vs. 1/B. The error in the slope was then calculated using the following equation

$$\text{Slope} \pm \frac{t_s}{\sqrt{\sum_{i=1}^{n} (x-\bar{x})^2}} \qquad (30)$$

where t is the student t statistic for n-2 degrees of freedom at a 80% confidence level, and s can be calculated as follows

$$S = \frac{\sum_{i=1}^{n} (y-\bar{y})^2 - \frac{\text{slope}}{n} \left[\sum_{i=1}^{n} xy - \left(\sum_{i=1}^{n} x \right) \left(\sum_{i=1}^{n} y \right) \right]}{n-2} \qquad (31)$$

The error in the intercept was calculated from the following equation

$$\text{intercept} \pm t_{\frac{1}{2}}^{2} V^{\frac{1}{2}} \left(\frac{1}{n} + \frac{x-\bar{x}^2}{\sum_{i=1}^{n} (x-\bar{x})^2} \right)^{\frac{1}{2}} \qquad (32)$$

where t is again the student t statistic for n-2 degrees of freedom at an 80% confidence level, and V_2 can be calculated as follows

$$V_2 = \frac{\sum_{i=1}^{n} (y-\bar{y})^2 - (\text{slope})^2 \left(\sum_{i=1}^{n} (x-\bar{x})^2\right)}{n-2} \qquad (33)$$

The error in the equilibrium constant can then be calculated from propagation of error methods. Since the equilibrium constant is calculated from the quotient intercept/slope the error in the equilibrium constant (σ_K) can be calculated as follows

$$\frac{\sigma_K}{K} = \left(\left(\frac{\sigma_S}{S}\right)^2 + \left(\frac{\sigma_I}{I}\right)^2\right)^{\frac{1}{2}} \qquad (34)$$

where S is the slope, σ_S is the error in the slope, I is the intercept, and σ_I is the error in the intercept. The equilibrium constant was then reported as $K \pm \sigma_K$.

CHAPTER 5

RESULTS, DISCUSSION AND CONCLUSIONS

Results

TABLE I

RETENTION TIME AND RELATIVE RETENTION TIME OF n-ALKANES ON EACH STATIONARY PHASE

Stationary Phase	Carbon Number	Retention Time (min.)	Relative Retention Time
Dimethylsilicone (SP-2100)	6	0.249	1.00
	7	0.513	2.06
	8	1.057	4.25
	9	2.200	8.84
	10	4.551	18.28
Phenylmethylsilicone (SP-2250,50% Phenyl)	6	0.129	1.00
	7	0.275	2.13
	8	0.616	4.77
	9	1.353	10.48
	10	3.023	23.42
Methylcyanopropylsiloxane (SP-2300, 36% Cyanopropyl)	8	0.447	1.00
	9	0.772	1.73
	10	1.202	2.69
	11	2.857	6.40
	12	6.457	14.45
Methylcyanopropylsiloxane (SP-2310, 55% Cyanopropyl)	8	0.500	1.00
	9	0.838	1.68
	10	1.753	3.51
	11	3.530	7.06
	12	6.972	13.94
Methylcyanopropylsiloxane (SP-2330, 68% Cyanopropyl)	9	0.323	1.00
	10	0.738	2.28
	11	1.596	4.93
	12	3.202	9.90
	13	7.702	23.82
Methylcyanopropylsiloxane (SP-2340, 75% Cyanopropyl)	9	0.049	1.00
	10	0.296	6.04
	11	0.857	17.52
	12	2.094	42.78

TABLE I (Continued)

Stationary Phase	Carbon Number	Retention Time (min.)	Relative Retention Time
Trifluoropropyl methyl silicone (SP-2401)	8	0.704	1.00
	9	1.391	1.98
	10	2.694	3.82
	11	5.255	7.46
	12	10.087	14.32
2-4% Aminoalkymethylsiloxane (PS-054)	6	0.362	1.00
	7	0.787	2.18
	8	1.696	4.69
	9	3.613	9.99
	10	7.594	20.99

TABLE II

LINEAR REGRESSION CONSTANTS FOR n-ALKANES $\log t_s = A + B$ (CARBON NUMBER)

Number	Stationary Phase	Temperature	Slope (B)	Intercept	Correlation Coefficient
1	Dimethylsilicone (SP-2100)	75°C	0.3160	-1.831	0.9999
2	Phenylmethylsilicone (SP-2250)	75°C	0.3431	-2.106	0.9999
3	Methylcyanopropylsiloxane (SP-2300, 36% Cyanopropyl)	75°C	0.2888	-2.039	0.9910
4	Methylcyanopropylsiloxane (SP-2310, 55% Cyanopropyl)	75°C	0.2913	-1.9895	0.9986
5	Methylcyanopropylsiloxane (SP-2330, 68% Cyanopropyl)	75°C	0.3391	-2.863	0.9995
6	Methylcyanopropylsiloxane (SP-2340, 75% Cyanopropyl)	75°C	0.5356	-5.348	0.9858
7	Trifluoropropylmethylsilicone (SP-2401)	75°C	0.2889	-1.788	0.9999
8	2-4% Aminoalkymethylsiloxane (PS-054)	75°C	0.3306	-1.748	0.9999

TABLE III

ACIDITY MEASUREMENTS: RELATIVE RETENTION TIME OF BUTYLAMINE WITH RESPECT TO BUTYLCHLORIDE

Number	Stationary Phase	Temperature	$\frac{t_s \text{ Butylamine}}{t_a \text{ Butylchloride}}$	Average	Standard Deviation	Log of Relative Retention Time
1	Dimethylsilicone (SP-2100)	75°C	0.972 0.919 0.914	0.935	0.0321	-0.0292
2	2-4% Aminoalkymethylsiloxane (PS-054)	75°C	1.01 1.02 1.06	1.03	0.0265	0.018
3	Phenylmethylsilicone (SP-2250, 50% Phenyl)	75°C	1.30 1.08 1.18	1.19	0.110	0.0755
4	Methylcyanopropylsiloxane (SP-2300,36% Cyanopropyl)	75°C	1.46 1.55 1.46	1.49	0.0520	0.173
5	Methylcyanopropylsiloxane (SP-2310, 55% Cyanopropyl)	75°C	1.83 1.61 1.66	1.70	0.115	0.230
6	Methylcyanopropylsiloxane (SP-2330, 68% Cyanopropyl)	75°C	1.75 1.62 1.72	1.70	0.0681	0.230
7	Trifluoropropylmethylsilicone (SP-2401)	75°C	3.12 3.95 3.42	3.50	0.420	0.544
8	Methylcyanopropylsiloxane (SP-2340, 75% Cyanopropyl)	75°C	4.83 4.14 3.62	4.20	0.607	0.623

TABLE IV

BASICITY MEASUREMENTS: RELATIVE RETENTION TIME OF ETHANOL WITH RESPECT TO ACETONE

Number	Stationary Phase	Temperature	$\frac{t_s \text{ Ethanol}}{t_s \text{ Acetone}}$	Average	Standard Deviation	Log of Relative Retention Time
1	Trifluoropropylmethylsilicone (SP-2401)	75°C	0.736 0.647 0.635 0.624 0.648	0.658	0.0447	-0.182
2	Dimethylsilicone (SP-2100)	75°C	0.855 0.932 0.865 0.707 0.873	0.864	0.0482	-0.0635
3	Methylcyanopropylsiloxane (SP-2300, 36% Cyanopropyl)	75°C	0.889 0.892 0.878 0.889 0.868	0.883	0.0100	-0.0540
4	2-4% Aminoalkymethylsiloxane	75°C	0.858 0.962 0.860 0.734 1.04	0.932	0.0744	-0.0306
5	Phenylmethylsilicone (SP-2250, 50% Phenyl)	75°C	1.09 0.975 0.899 0.914 0.856	0.947	0.0907	-0.0236

TABLE IV (Continued)

Number	Stationary Phase	Temperature	$\frac{t_s \text{ Ethanol}}{t_s \text{ Acetone}}$	Average	Standard Deviation	Log of Relative Retention Time
6	Methylcyanopropylsiloxane (SP-2340, 75% Cyanopropyl)	75°C	1.11			
			1.10			
			1.12	1.11	0.00816	0.0453
			1.11			
7	Methylcyanopropylsiloxane (SP-2330, 68% Cyanopropyl)	75°C	1.13			
			1.19			
			1.17	1.17	0.0261	0.0681
			1.19			
			1.19			
8	Methylcyanopropylsiloxane (SP-2310, 55% Cyanopropyl)	75°C	1.26			
			1.26			
			1.23	1.24	0.0187	0.0934
			1.23			
			1.22			

TABLE V

NMR ACIDITY MEASUREMENTS WITH QUINUCLIDINE $\frac{1}{\delta_{obs}} = \frac{1}{[B]} \cdot \frac{1}{K\delta_{obs}} + \frac{1}{\delta_{AB}}$ $K = \frac{\text{Intercept}}{\text{Slope}}$

Number	Stationary Phase	Quinuclidine Concentration	Proton Resonance Position (ppm)	Linear Regression Data			Equilibrium Constant
				Slope	Intercept	Correlation Coefficient	
1	Dimethylsilicone SP-2100			0			0
2	2-4% Aminoalkymethylsiloxane (PS-054)			0			0
3	Phenylmethylsilicone (SP-2250, 50% Phenyl)			0			0
4	Methylcyanopropylsiloxane (SP-2310, 55% Cyanopropyl)	0.5006 1.001 1.499 2.001 2.501	1.782 1.817 1.827 1.849 1.856	0.01334 ±0.002997	0.5355 ±0.003315	0.9715	40.14 ± 9.02
5	Methylcyanopropylsiloxane (SP-2300, 36% Cyanopropyl)	0.5018 1.000 1.499 2.000 2.499	2.155 2.183 2.190 2.204 2.215	.006346 ±0.002742	0.4514 ± 0.002930	0.9112	71.13 ± 30.74

TABLE V (Continued)

Number	Stationary Phase	Quinuclidine Concentration	Proton Resonance Position (δ, ppm)	Linear Regression Data			Equilibrium Constant
				Slope	Intercept	Correlation Coefficient	
6	Methylcyanopropylsiloxane (SP-2330, 68% Cyanopropyl)	0.5002 0.9996 1.500 1.999	1.764 1.775 1.792 1.796	±0.007634 ±0.002581	0.5528 ±0.003038	0.9319	72.41 ±24.48
7	Trifluoropropylmethylsilicone (SP-2401)						?
8	Methylcyanopropylsiloxane (SP-2340, 75% Cyanopropyl)	0.5006 1.000 1.500 2.501	1.775 1.778 1.782 1.789	0.002385 ±0.001861	0.6691 ±0.002027	0.8803	234.4 ±182.9

TABLE VI

NMR BASICITY MEASUREMENTS WITH CHLOROFORM $\frac{1}{\delta_{obs}} = \frac{1}{[B]} \cdot \frac{1}{K\delta_{AB}} + \frac{1}{\delta_{AB}}$ $K = \frac{\text{Intercept}}{\text{Slope}}$

Number	Stationary Phase	Stationary Phase Concentration	Proton Resonance Position (δ ppm)	Linear Regression Data Slope	Intercept	Correlation Coefficient	Equilibrium Constant
1	Trifluoropropylmethylsilicone (SP-2401)	1.999 2.249 2.349 2.499	7.338 7.373 7.387 7.394	0.01121 ± 0.009840	0.1307 ± 0.0007753	0.9950	11.66 ± 10.24
2	Dimethylsilicone (SP-2100)	2.002 2.249 2.348 2.500	7.275 7.303 7.310 7.317	0.008315 ± 0.004513	0.1333 ± 0.0001024	0.9756	16.03 ± 8.01
3	Methylcyanopropylsiloxane (SP-2310, 55% Cyanopropyl)	1.998 2.150 2.249 2.349 2.499	7.493 7.514 7.521 7.528 7.535	0.008021 ± 0.004787	0.1294 ± 0.0006647	0.9840	16.13 ± 9.63
4	Methylcyanopropylsiloxane (SP-2300, 36% Cyanopropyl)	2.001 2.150 2.250 2.500	7.387 7.394 7.408 7.423	0.007138 ± 0.005290	0.1318 ± 0.0005422	0.9968	18.46 ± 13.68
5	Methylcyanopropylsiloxane (SP 2340, 75% Cyanopropyl)	2.001 2.149 2.250 2.349 2.500	7.401 7.408 7.415 7.430 7.447	0.006491 ± 0.002959	0.1319 ± 0.0008976	0.9542	20.32 ± 9.26

TABLE VI (Continued)

Number	Stationary Phase	Stationary Phase Concentration (M)	Proton Resonance Position (δppm)	Linear Regression Data			Equilibrium Constant
				Slope	Intercept	Correlation Coefficient	
5	Methylcyanopropylsiloxane (SP-2340, 75% Cyanopropyl)	2.001 2.149 2.250 2.349 2.500	7.401 7.408 7.415 7.430 7.437	0.006491 ±0.002959	0.1319 ±0.0008976	0.9542	20.32 ±9.26
6	Phenylmethylsilicone (SP-2250, 50% Phenyl)						?
7	2-4% Aminoalkymethylsiloxane (PS-054)	1.500 1.600 1.700 1.800	7.440 7.451 7.461 7.472	0.004438 ±0.003814	0.1314 ±0.002497	0.8226	29.61 ±25.45
8	Methylcyanopropylsiloxane (SP-2330, 68% Cyanopropyl)	2.000 2.149 2.249 2.500	7.373 7.380 7.387 7.394	0.004063 ±0.006199	0.1336 ±0.0004970	0.9940	32.88 ±50.16

TABLE VII

CORRELATION BETWEEN NMR AND GC DATA

A. Acidity Measurements

Stationary Phase	Equilibrium Constant	Log of Relative Retention Time
Methylcyanopropylsiloxane (SP-2300, 36% Cyanopropyl)	71	0.173
Methylcyanopropylsiloxane (SP-2310, 55% Cyanopropyl)	40	0.230
Methylcyanopropylsiloxane (SP-2330, 68% Cyanopropyl)	72	0.230
Methylcyanopropylsiloxzne (SP-2340, 65% Cyanopropyl)	230	0.623
Correlation Coefficient	0.97	

TABLE VII (Continued)

B. Basicity Measurements

Stationary Phase	Equilibrium Constant	Log of Relative Retention Time
Trifluoropropylmethylsilicone (SP-2401)	12	-0.182
Dimethylsilicone (SP-2100)	16	-0.0635
Cyanopropylmethylsiloxane (SP-2300, 36% Cyanopropyl)	18	-0.0540
Cyanopropylmethylsiloxane (SP-2310, 55% Cyanopropyl)	16	0.0934
Cyanopropylmethylsiloxane (SP-2330, 68% Cyanopropyl)	33	0.0682
Cyanopropylmethylsiloxane (SP-2340, 75% Cyanopropyl)	20	0.00816
2-4% Aminoalkymethylsiloxane (PS-054)	30	-0.0306
Correlation Coefficient		.50

Gas Chromatographic Work

The gas chromatographic work that has been accomplished here establishes the ground work for a new and different method for the classification of liquid stationary phases. This method is no more difficult to use than any of the previous attempts at classification schemes but it provides something that they do not. It is very easy to interpret. The interpretation of this classification scheme has been simplified by completely separating the different types of interaction that a liquid phase can undergo. When complete tables of dispersion, polarity, acidity, and basicity indices are developed for the most popular stationary phases one of the most difficult problems the chromatographer faces can be greatly simplified. This simplification would lead to the expansion of the field of chromatography to those who have need of the technique but lack the experience to solve some of the more difficult problems.

Probe Pairs

The choice of the probe pairs in this work is critical. Decisions about the choice of the probe pairs were based on the published tables of Kirkland.[28] The properties of butylchloride and butylamine were assumed to follow very closely to the properties of propyl chloride and propylamine.

The identical dispersion interactions and widely varying basicities were perfect for the acidity measurements. However, the slight differences in the polarities and acidities might cause some slight problems. The dominant effect, and the main cause of the separation of butylchloride and butylamine will be the basicity of the butylamine with only small contributions from the acidity and polarity.

The choice of ethanol and acetone as a probe pair for basicity does not appear to be the perfect choice. The dispersion and acidity indices are fine and the slight difference in the polarities can be tolerated but there is a significant difference in the basicities that can not be ignored. Even though the difference in acidities will be the dominant interaction for separating these two solutes there will be some overlap with the basicity interaction. This could not be avoided because of the reliance on the published tables of solubility parameters. The ethanol/acetone pair was among the best choices for the probe pair. In order to improve the choice of a probe pair it would be necessary to increase the number of compounds with known solubility parameters. Such work was beyond the scope of this thesis.

Homologous Series of n-Alkanes

A homologous series of n-alkanes was run on each of the columns. A linear regression analysis was then

completed for the equation

$$\log t_s = A + B \text{ (carbon number)} \qquad (35)$$

The relatiohship between the logarithm of the retention time vs. the carbon number should be linear and was used to indicate if the columns were in proper working order. As can be seen in Table II the correlation coefficients are sufficiently close to one that it can be assumed the columns are working properly. In addition to this use Rohrschneider[63] observed that the magnitude of the slope of these lines could be used as a measure of the polarity of the stationary phase. This also was beyond the scope of this thesis.

Discussion of Acidity Results

The acidity results of Table III exhibit roughly what was expected. This is probably due to the close match in properties between the butylchloride and butylamine. The relative retention times of dimethylsilicone and aminoalkymethylsiloxane are close enough to one that they can be considered to be nonacidic. The relative retention time of 0.935 for the dimethylsilicone might be the result of a slight difference in the dispersion, polarity, or acidity index for butylchloride and butylamine.

Since there are no obvious proton donors among the

remaining group of stationary phases, their acidity can best be thought of as Lewis acidity. The slightly acidic relative retention time of 1.19 for phenylmethylsilicone probably reflects the attraction of the lone pair electrons of the amine group of butylamine by the aromatic ring of the phenyl group. In addition to the cyano group of the methylcyanopropylsiloxane being polar it could also act like a Lewis acid group by attracting the lone pair electrons of the amino group. It is also possible that the high polarity of the C≡N would cause the adjoining $-CH_2-$ to act like a Bronsted acid. The acidity of the cyanopropyls also increases as the percentage of the cyano group increases just as would be expected. The only unusual thing is the unusually high relative retention time of the 75% cyanopropyl when compared to the other members of the cyanopropyl group.

The high relative retention time of the probe pair on the trifluoropropylmethylsilicone reflects fairly high acidity. This acidity could be of the Lewis type if the high electronegativity of the trifluoro group is attracting the lone pair electrons of the amino group. As was stated above, it is also possible that Bronsted acidity is being exhibited by the adjacent $-CH_2-$ group. Since the NMR method requires that a hydrogen bond be formed, a high acidity value from the NMR method would confirm the Bronsted acidity over the Lewis acidity.

Discussion of Basicity Results

Unlike the acidity measurements where the experimental results follow predicted patterns, the basicity measurements seem to be very unpredictable. This problem is most likely caused by the overlap of acidity and basicity interactions which makes interpretation very difficult. However, this provides a good example of the difficulty in interpreting the previous classification schemes which have overlapping interactions in the indices that they report.

It would normally be expected that the dimethylsilicone, aminoalkymethylsiloxane, and phenylmethylsilicone would be among the least basic of the stationary phases under study. The dimethylsilicone should be the least basic of the group because of its lack of ability to either donate electrons or form a hydrogen bond. I would assume that the aminoalkymethylsiloxane would follow the dimethylsilicone on the basicity scale. Even though it has a basic amino group, the low percentage (2-4%) of that group would make it only slightly basic. I would also expect the phenylmethylsilicone to be only slightly basic. The slightly basic nature might arise from an attraction of the hydroxyl proton of ethanol towards the aromatic ring.

We know that the trifluoropropylmethylsilicone is very acidic when compared to the other stationary phases under study. This high acidity is probably the reason that the acetone is held longer on the column than it should be.

However, it is possible that the fluorine molecules can form a hydrogen bond, as it does in HF, with the hydroxyl proton of the ethanol. If this could happen the trifluoro silicone would exhibit some basicity. However, Burns and Hawkes[27] found no basicity for the trifluoro silicone. At any rate the basicity, if any, of the trifluoropropyl-silicone would probably be comparable to that of the amino-alkymethylsiloxane and the phenylmethylsilicone.

The methylcyanopropylsiloxanes seem to be completely out of order. As was the case of the acidity measurements, one would expect that the basicity of the cyanopropyls would increase with increasing percentages of the cyano group. Instead of a linear relationship the experienced relationship is more parabolic. The 36% cyanopropyl is weakly basic, the 55% cyanopropyl is the most basic, 68% cyanopropyl is less basic than the 55% cyanopropyl, and the basicity of the 75% cyanopropyl is between that of the 36% and 68% cyano-propyls. What may actually be causing this parabolic effect is an overlap of acidity and basicity interactions. The 36% cyanopropyl, having the lowest acidity of the group would also have the least amount of overlap between the acidity and basicity interactions. It should be where it is as the least basic of the cyanopropyls. The 55% cyano-propyl has an increased amount of the cyanopropyl group and should be more basic than the 36% propyl. The overlap

of interactions begins to cause problems with the 68% cyanopropyl. Since the 68% cyanopropyl has more of the basic cyanopropyl group it should theoretically be more basic. However, it is also fairly acidic. What has happened here is that the 68% cyanopropyl is probably more acidic than it is basic. Because of its stronger acidity it will tend to retain the acetone longer than the 55% cyanopropyl would, thereby making it appear to be less basic. The 75% cyanopropyl, being a much stronger acid, would tend to exhibit this behavior to a larger extent which it has been shown to do experimentally. Actually, when considering the standard deviations of the relative reteniton times of the 55% and 68% cyanopropyls,their acidities and basicities are not statistically different. The crossover point where the acidity overcomes the basicity could occur anywhere from 50% to 70% of the cyanopropyl group. These problmes probably would not occur if a more closely matched probe pair could be found.

This problem with the cyanopropyls is a good example of what can occur when a classification scheme reports indices which possess an overlap of interactions. The interpretation becomes very difficult and many assumptions must be made. The acidity measurements however were very straightforward and easy to interpret. As was stated before in this chapter, to eliminate this problem with the basicity measurements,

solubility parameters for more compounds than were listed by Kirkland[28] would have to be derived and the properties of the probe pair would have to be matched more closely. The only alternative would be to derive some correction factor that would compensate for the difference in basicities of ethanol and acetone.

Nuclear Magnetic Resonance Spectroscopic Work

Nuclear magnetic resonance spectroscopy was used in addition to the gas chromatographic approach for determining the acidity and basicity of liquid stationary phases. The main purpose for this was to attempt to relate the relative retention time directly to a measure of the strength of the acidity or basicity. NMR methods were found to directly calculate the equilibrium constant for the formation of a hydrogen bond between the stationary phase and either an acid or a base. It was hoped that these equilibrium constants would then directly correspond to the relative retention time data.

Choice of Solvents

One of the more difficult decisions that had to be made in the NMR work was the choice of a proper solvent. Carbon tetrachloride was the perfect choice because it doesn't have a proton resonance peak, it has no anisotropy,

was shown to have negligible acidity or basicity, and has no polarity. The only problem was that the stationary phases that were chosen for this work were not soluble in CCl_4. This problem forced the use of a less desirable solvent. The major requirements that had to be fulfilled were the absence of acidity or basicity and the absence of a proton resonance peak in the area of the hydrogen bonded proton's resonance peak. Problems with anisotropy and other solvent effects would have to be tolerated. Initially deuterated solvents were thought of as the solution to the problem. However, due to their cost it was not possible to obtain them for this work.

For the basicity measurements 1,1,1 trichloroethane was chosen as the solvent. This solvent has negligible acidity or basicity and the chemical shift of its proton resonance peak was located several ppm upfield from that of the hydrogen bonded proton. The molecule is polar and will possess some anisotropy but these problems were unavoidable.

The acidity measurements were accomplished with chlorobenzene as the solvent. 1,1,1 trichloroethane could not be used as the solvent because the chemical shift of its proton resonance peak is in the same area as that of the hydrogen bonded proton. Since the solvent peak is much larger it must be at least several ppm away from the hydrogen bonded proton's resonance peak. In order to be far

enough away it was necessary to use a solvent that only had resonance peaks in the area where highly polar or aromatic compounds are located. Chlorobenzene was chosen because of its low acidity and basicity when compared to other compounds that have peaks in that area despite having problems similar to those of the 1,1,1 trichloroethane. There would be more anisotropy because of the aromatic ring and other solvent effects would occur but as before the problems were unavoidable.

As was stated previously the effects of the solvent on the NMR spectrum due to Van der Waals forces, anisotropy, and polarity were said to cancel out due to experimental conditions and the method of calculating the equilibrium constants. The equilibrium constant is calculated from intercept/slope for a plot of $1/\delta_{obs}$ vs. $1/[B]$. Only the $1/\delta_{obs}$ term would be affected by solvent effects. Assuming that the solvent effects for a given set of solutions for one stationary phase are constant as the concentration of the base is changed; the magnitude of the shift in the resonance position will be the same for each of the solutions. If this magnitude of the shift is constant for each of the solutions, the slope of the line will not be altered. The intercept however, would be slightly altered. Since the stationary phases that are being worked with have many similar properties, especially when compared with the large

number of phases that were not studied, the magnitude of the shift caused by the solvent effects would be similar for each of the stationary phases. The calculated equilibrium constants would be accurate only when compared to the other equilibrium constants obtained in this thesis. The small error in the intercepts reported in Tables V and VI supports this assumption. Large errors in the intercepts would relate to a large difference in the solvent effects that each stationary phase experiences. Therefore for this case the solvent effects can be largely ignored if it is remembered that the calculated equilibrium constants can only be used relative to each other and the actual values have little meaning when compared to other systems developed by other researchers. This could be a serious defect if it is not remembered that this thesis is merely attempting to develop a new method for classifying stationary phases and not generating the actual numbers for the tables of the classification scheme. I feel the method is sound and with sufficient funds to purchase the proper solvents the results would be very reliable.

Choice of Acid and Base

The choice of an acid for basicity measurements and a base for the acidity measurements was made primarily on the basis of the published work of other researchers.

The most common choices for the acids were phenol and chloroform. Phenol was chosen at first because it seemed to be more popular in the literature. However a strange thing happened, the hydrogen bonded proton's resonance peak for the stronger bases completely disappeared and for the other stationary phases the peak shrank as the concentration of the stationary phase increased. Eventually the peak was lost in the noise at the highest concentrations. This effect was thought to be caused by the strength of the phenol and the weak base nature of the stationary phase. The mismatched acid base pair was preventing the desired 1:1 hydrogen bonded complex from forming. When the weak acid chloroform was substituted for the phenol, the problem disappeared completely. Chloroform was then used as the acid for all of the basicity measurements with no further problems.

Quinuclidine was used as the base for acidity measurements. This choice was based on the work of Slejko and Drago.[66] No problems arose with its use and its seemed to work fine.

Discussion of Acidity Results

For the most part the acidity results correspond with what was expected. Dimethylsilicone, aminoalkymethylsiloxane, and phenylmethylsilicone exhibited no acidity.

This lack of acidity was observed by the failure of any of the resonance peaks to shift as the concentration of the quinuclidine was increased. The small difference in acidity that was observed in the gas chromatographic data for the phenylmethylsilicone was not observed here possibly due to the greater sensitivity of the gas chromatographic method. Possibly a more powerful NMR spectrometer would eliminate this discrepancy.

It was not possible to measure the acidity of the trifluoropropylmethylsilicone since the small hydrogen bonded resonance peak could not be observed because it was approximately in the same position as the much larger quinuclidine peaks.

The only unusual occurrence is that the 36% cyanopropyl has a larger equilibrium constant than the 55% cyanopropyl. Even though at first glance the difference in the equilibrium constants seems significant, when one takes the error in the equilibrium constants into account the two are not statistically different.

The alarming problem with these results are the large errors associated with the equilibrium constants. These large errors are associated with the large errors in the slope. As was explained in the choice of solvent section of this chapter, I do not feel that this problem is due to any solvent effects. The solvent effects of a 2.0 M

solution of quínuclidine should not be significantly different from the solvent effects in a 1.0 M quinuclidine solution. The only significant difference is the concentration of the quinuclidine. Though quinuclidine was chosen for its low anisotropy, its Van der Waals forces and polarity could be causing the problem. If this is the case then a correction factor would have to be determined to eliminate the error.

A more likely answer to this problem is the NMR spectrometer that was used. The 60 MHz instrument that was used was not kept in a temperature controlled room. This led to problems with the spectrometer not being very well tuned up for the most part. A more powerful instrument would provide better resolution. Also if the instrument was under computer control it could directly read out the chemical shift without the error associated with measuring the chemical shift by hand. I feel the better instrument would eliminate most of the error associated with measuring the chemical shift and therefore the slope. Due to the large number of samples (80-100) and the insufficient funds it was impossible to send the samples out to be run on another outside instrument or to have them run on the chemistry department's more powerful instrument.

Discussion of Basicity Results

The NMR basicity measurements appear to fairly closely resemble the gas chromatographic basicity rankings. However, when one looks at the error in the equilibrium constants it can be seen that none of the measurements are statistically different from each other at the 80% confidence level. One of the values, the 68% cyanopropyl, is not even statistically different from zero. No measurements were made on the phenylmethylsilicone because the hydrogen bonded peak was wiped out by the phenyl protons from the stationary phase. The major culprit again is the slope of the line. Reasons for this error were discussed in the previous section and will be addressed further in the final section.

Correlation between the G.C. and the NMR Data

Though any relationship between the gas chromatographic and the NMR data must be taken with a grain of salt, correlation coefficients were calculated between the logarithm of the relative retention time and the equilibrium constants. Because of the unreliability of the NMR data, only the average values were used with no correction for the large amount of error.

The acidity measurements show a fairly good correlation coefficient of 0.97. This value probably reflects

the gas chromatographic acidity measurements more than the NMR data. This also shows that there could be some hope for relating these two different appraoches in the future.

The rather poor correlation coefficient for the basicity measurements of 0.50 probably reflects the overlap of interactions in the gas chromatographic method along with the poor reliability of the NMR data.

Conclusions

Many problems were encountered in the compilation of this research. Some of them were solved, others were not. I feel that the main cause of the unsolved problems was the insufficient funding available for materials and access to better instrumentation. Adequate funding might have led to the solution of these problems and then again it might have led to other problems down the line that will be left for other researchers to discover.

The stationary phases that were chosen to work with could also be the cause of some of the problems. The acidity and basicity of the silicone based stationary phases are much lower than those of the majority of other stationary phases. This low acidity and basicity could have been at or near the limit of detection of the NMR method for the detection of a hydrogen bonded proton in a hydrogen

bonded complex. This could have led to some of the unreliability in the NMR measurements.

The methods that were developed for this research are based on a sound theoretical foundation. The Benesi-Hildebrand equation has been in use for several years and has been quite widely accepted. The only problem with it is the numerous experimental bugs. There are too many variables and not enough is known about all of them to have a completely controlled experiment at this time. Some day it will happen because the method is a good one.

The use of the relative retention time of a probe pair that is specific for a particular type of interaction is also a good technique. The basicity measurements showed how difficult it is to interpret classification schemes that have mixed interactions in their indices as most of the published schemes have today. The acidity measurements showed how simple the classification scheme can be if the indices reflect only one type of interaction.

Even though some of the data that was obtained here is not too reliable, it is not the fault of the methods that were involved. The methods are good ones and deserve further investigation. The problems in the experimental conditions could be overcome with additional funding. Under the circumstances of little funding I feel that the

best job was accomplished using the available materials and instrumentation.

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