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Date August 1990

MOLECULAR RECOGNITION MECHANISMS DISPLAYED BY POLYMER-SUPPORTED REAGENTS: FOURIER TRANSFORM INFRARED STUDIES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Rosario Munoz-Martinez

August 1990

DEDICATIONS

To my mother CARMEN, my family and my Latin American friends for their encouragement and moral support during my studies.

ACKNOWLEDGMENTS

I would like to thank Dr. Spiro D. Alexandratos for being my Major Professor and for his encouragement and support during my studies at UTK, and Dr. George K. Schweitzer for his assistance as my International Advisor. I would also like to thank Dr. Earl Wehry and Dr. Michael Sepaniak for participating in my Master's Committee, and The University of Tennessee, Knoxville, The University of Cartagena (COLOMBIA) and FULBRIGHT-LASPAU for the financial support during my studies in U. S. A.

ABSTRACT

Polymer-supported reagents have experienced increasing popularity during the last twenty years (within chemistry). There are many advantages realized by binding a chemically reactive species to an insoluble support. Polymer-supported reagents have many applications in fields such as organic and inorganic chemistry, biochemistry and biology.

A Fourier Transform Infrared (FTIR) study of the soluble analogues of polymer-supported reagents (synthesized in Dr. Alexandratos' laboratory) interacting with various target compounds was carried out. The complexation mechanisms displayed by the polymeric reagents were thus elucidated through model compound studies. Along these lines, the interaction of substituted anilines with polymeric phosphinic acid was investigated by FTIR studies of those anilines with phenyl phosphinic acid.

The FTIR analysis shows that phenyl phosphinic acid is an intermediate compound between the strong methanesulfonic acid and the weak benzoic acid, when reacting with aniline. By analogy, polymeric sulfonic acid displays a stronger interaction with aniline than polymeric phosphinic acid. However, the latter resin provides a better understanding of substituent effects when reacting with substituted anilines.

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CHAPTER I

INTRODUCTION

The high resolution possible in Fourier transform infrared (FTIR) analysis is a very important tool used to comprehend the interactions displayed by polymer-supported reagents with molecular species.

The separation of molecular or ionic species from aqueous solutions is important for chemical and environmental purposes. Polymer-supported reagents have been used lately as substrates for metal ion separations.[1,2] It is possible to recover metal ions such as copper, silver, gold, and mercury by using supported resins. Some of these resins are the following:

1) Supported hydroxyoximes
2) Sulfur-containing resins such as polystyrene-supported dithiocarbamate derivatives
3) Arsonic acid resins
4) Polyethyleneimine resins which are used to recover uranium from sea water.[3-7]

Nuclear industry is interested in removing radioactive ions from water. This process is necessary for a clean environment. Ion exchange resins can be used to remove these ions.[8]

When a polystyrene network reacts with sulfuric acid it yields the strong polymeric sulfonic acid, a cation exchange resin.[1,9] This resin is used to recover metals but has no selectivity due to the extended range of metals absorbed.[1]

A resin with enhanced selectivity is required to recover a particular metal ion under a broad range of experimental circumstances.[1] While polymeric sulfonic acid absorbs metal ions without selectivity,[1,10] weak carboxylic acid resins display selectivity for multivalent ions, but these resins require a restricted pH range.[11-13]

Looking for the ideal ion exchange resin, phosphorus-based resins have been utilized lately in solvent extraction chemistry.[14] The phosphorus acid ligand has an intermediate acidity between sulfonic and carboxylic acid ligands;[15,16] therefore, it can display higher selectivity.[1]

The polymeric phosphinic acid is being studied in the laboratory of Professor S. D. Alexandratos as an element of dual mechanism bifunctional polymers, designed and developed for selective metal ion extraction[17]. Polymeric phosphinic acid contains the phosphinic acid ligand. This ligand is bound to the polystyrene/divinylbenzene copolymer, which is the support.

Due to the strong acidity of polymeric sulfonic acid and the intermediate acidity of polymeric phosphinic acid, this research is concerned with the bond and the strength,

that these two polymer-supported reagents undergo with particular molecules.

The interaction between polymer-supported reagents and molecules is primarily analyzed with a selected group: aniline and its derivatives (p-methoxyaniline and m-chloroaniline). The formation of a hydrogen bond is feasible among the OH groups of both polymers and the N of the amino group of aniline. The hydrogen bond, in this case O-H···N, is the bond in which a hydrogen atom is placed between two closely spaced electronegative atoms; in a general sense, it is the interaction between an A-H group of a molecule with a B atom, frequently of another molecule. The A-H group is described as a proton donor and the B atom as the proton acceptor. The atoms involved in hydrogen bond formation are usually oxygen, nitrogen, fluorine, and sporadically chlorine.[18,19]

Because the force field nearby the hydrogen atom is modified as a consequence of the formation of the new bond, the A-H vibrational bands are also modified. The A-H stretching band, which is commonly sharp in a free state, becomes very broad and is shifted to lower frequencies upon the formation of a hydrogen bond. The A-H bending vibrations rise in frequency upon the formation of a hydrogen bond; this is the opposite shift of the stretching vibration. Vibrations involving the B atom may be changed as the result of the hydrogen bond.[19]

The quantity of the A-H frequency shift is related to the A····B distance; the shorter the distance, the bigger the shift. In addition, the higher the acidity of A-H and the higher the basicity of B, the stronger the hydrogen bond between A and B, and the smaller the distance between A and B.[19]

The formation of a hydrogen bond alters numerous properties when it takes place in a solution or a compound. Hydrogen bonds can exist within molecules and between molecules. Hydrogen bond compounds thus display weak bonds and extraordinary properties. The structure of proteins is explained by hydrogen bonding. Enzyme activity, catalysis, kinetics, dyeing and adsorption are considered among the fields of application of hydrogen bonding. All of the properties of water, physical and chemical, are affected by hydrogen bonds. Consequently, the hydrogen bond is one of the most important bonds in nature. It could be considered as significant as the carbon-carbon bond.[18]

Regarding aniline derivatives, methoxy is an activating group of the benzene ring because of its resonance effect. As a result, para-substitution of methoxybenzene in a given reaction is faster than substitution on benzene. On the other hand, chlorine is a deactivating group of the benzene ring because of its inductive effect. The resonance effect of chlorine is weak, and meta-substitution in halobenzenes is deactivated even more than para-substitution.

The activating effects of substituent groups must be taken in consideration for a given reaction.[20]

Since the substituent groups in aniline have opposing effects, it is expected that a stronger hydrogen bond exists between the polymer-supported reagents and p-methoxyaniline than the bond between the polymer-supported reagents and m-chloroaniline.

All of the polymer-supported reagent interactions are studied through model compounds. The selected model for polymeric sulfonic acid is the single molecule methanesulfonic acid, and for polymeric phosphinic acid, phenyl phosphinic acid is selected. The polymer and the single molecule present an equal reactive group. Therefore, a similar form of interaction could be a possibility for both the model compound and the polymer-supported reagent.

Polymeric sulfonic acid interaction with aniline is presented in this thesis (FTIR spectra and peak analysis). In the same manner, its interaction is compared with substituted anilines. The substituent effect is thus studied. Polymeric phosphinic acid interactions with aniline and aniline derivatives are also presented, as well as the differences that polymeric phosphinic acid might present in comparison to polymeric sulfonic acid. The fact that the phosphinic ligand has an intermediate acidity, and the sulfonic ligand has a strong acidity, make the interactions different if considering the hydrogen bond as the outcome

of those interactions.

It is important to understand how polymer-supported reagents interact with molecules. Infrared spectroscopy is a technique that detects any vibrational change that occurs in a polymer-supported reagent when interacting with another molecule.

Fourier transform infrared spectroscopy as a high resolution technique facilitates the analysis of polymer-supported reagents' interactions with single molecules presented in this thesis.

CHAPTER II

INFRARED ANALYSIS OF POLYMERS

Infrared spectroscopy is an old technique used for the characterization of molecules; it has also been used to analyze polymer systems.[21-23] Infrared spectroscopy is a non-destructive, simple technique. Solids, liquids, and gases can be analyzed, and qualitative as well as quantitative measurements can be made in a complex mixture.[22]

Although infrared spectroscopy is a low-energy technique, useful data are obtained from infrared spectra.[22] The range of applications has been increased with the advantages of the FOURIER TRANSFORM INFRARED (FTIR) spectroscopy.[21-23]

The basic optical component of the FTIR instruments, the Michelson interferometer, provides great advantages such as reduced time and improved signal to noise ratio.[21-25] Today modern scanning FTIR spectrometers obtain the data necessary for a complete infrared spectrum within seconds. The signal, obtained from the detector, is called an interferogram and carries all the necessary data to reproduce the spectrum via the mathematical process well-known as Fourier transformation.[24,25]

Infrared spectra can be obtained by either dispersive

or interferometric methods. The dispersive instruments record the spectrum in the frequency domain, while the interferometers record the spectrum in the time domain; then, the spectrum is converted to frequency domain by applying Fourier transformation.[26] As mentioned before, the two prominent advantages of interferometers over dispersive spectrometers are sensitivity and speed. These advantages are the consequences of Fellgett's advantage (multiplex advantage) and Jacquinot's advantage (increased throughput). As all the frequencies are measured simultaneously in interferometry, the spectra can be acquired much faster and the S/N ratio can be improved for a given resolution.[24-26]

Infrared spectroscopy provides information on molecular structure through the frequencies of the vibrations of the molecule. Bands (also called peaks, when they are sharp and narrow) for functional groups, usually encountered in organic compounds, are located in the wavelength range 4000 to 400 cm^{-1}. [23,26]

Infrared studies have been described as "*the* most sensitive, *the* most characteristic, and *one of the* most informative manifestations of the hydrogen bond" (Hiebert *et al.* quoted by Pimentel, G. and Mc. Clellan, A., 1960).[18,27,28] Many deductions can be assumed by considering changes in the vibrational spectrum of a compound.[28] The change in frequency is a magnitude of the strength of the hydrogen bond. Molecular geometry, ring strain, and

the relative acidity and basicity of the compounds affect the strength of the bonding.[29]

The application of infrared spectroscopy to the structure analysis of polymeric systems is well known as seen by the number of papers in the field recently. Because of the direct interfacing a computer to a spectrometer, the spectra can be worked in different ways; for example, interfering absorbances are removed by subtracting them from complex spectra. An interesting application of FTIR spectroscopy is the spectral separation of a complex spectrum of a heterophase system. One illustration is a semicrystalline polymer which may be observed as a complex system containing an amorphous and crystalline phase.[30]

The presence of a hydrogen bonded network in polymers, such as nylon 66, has been already studied by FTIR analysis. As a result, many of the physical and mechanical properties of the polyamides have been attributed to this bond.[21]

Another interesting application of FTIR analysis to polymers is the mechanism of the ultraviolet degradation of polyethylene, which compares the infrared spectrum of a semicrystalline PE irradiated film, with the spectrum of the unirradiated sample. The photochemical degradation of polymers is important because these compounds, especially those utilized in outdoor applications, might be altered by ultraviolet rays from the atmosphere. Among them is

polyethylene, which is a high volume commercial polymer.[30] Other FTIR studies have evaluated the interaction of anti-oxidants in butadiene rubbers and the effects of several additives on cure.[22]

The characterization of polymers by infrared spectroscopy represents one particular utilization of the group frequency notion. The spectrum of a single unit in a homopolymer is identical with that of a long chain of the same units. With copolymers, the spectrum is more difficult to interpret because of unlike units.[23]

The most important regions for an introductory test of a spectrum are two: 4000-1300 cm^{-1}, named the functional group region, and 900-650 cm^{-1}, where aromatic compounds usually absorb strongly. The intermediate region of the spectrum, 1300-900 cm^{-1}, is commonly named the "fingerprint" region because of the complicated absorption pattern.[29]

Lambert *et al* (26) and Silverstein *et al* (29) include tables of characteristic group frequencies after following the examinations of many compounds in which the groups occur.

Among the most important frequencies for spectrum analysis are the following:

Frequency Average (cm^{-1})	Functional Group
3700-3100	OH (alcohols and phenols) NH (amines and amides)

Frequency Average (cm^{-1})	Functional Group
3100-3000	CH (aromatic)
3000-2800	CH (aliphatic)
2500	PH, SH
2000-1800	Weak bands benzene deriv. Vinyl, vinylidene
1700	CO
1600	NH, NO_2, C=N, C=C
1200	C-O-C (ethers and esthers) C-OH (alcohols and phenols) S=O, P=O, C-F
800	=CH, Vinyl, Vinylidene, Aromatic NH_2 and NH (amines and amides)
600	C-Cl, C-Br

The tables from Lambert *et al* (26) and Silverstein *et al* (29) were the guide to analyze and elucidate all of the peaks in each FTIR spectrum presented in this thesis.

CHAPTER III

EXPERIMENTAL SECTION

* FTIR Analysis of Model Compounds.

The model compounds study begins with the selection of the compounds' concentration, the choice of the right solvent for the investigation including the polymer-supported reagents and the choice of cell for the FTIR study.

The following represents the optimized conditions:

1) SOLVENT: Benzene-Methanol in a 75/25 volume ratio (BM-75).
2) ANILINE CONCENTRATION: 4 Normal.
3) METHANESULFONIC ACID (MSA) CONCENTRATION: 0.8 Normal.
4) CELL: Minicell with AgBr windows.

When all of these factors are selected, the research starts with the first interaction.

Aniline : Methanesulfonic Acid.

To prepare 5 mL of 4N BM-75 solution of aniline (FW 93.13), 1.8626 g are accurately weighed and deposited in a 5 mL volumetric flask, dissolved in benzene-methanol (75/25), prepared previously. To prepare 25 mL of 0.8N BM-75 solution of methanesulfonic acid (FW 96.10), an accurately weighed sample of 1.9220 g is dissolved in BM-75 in a 25 mL volumetric flask.

With these two solutions and BM-75, three dilutions (1.5 mL each) are prepared as follows:

	A/M	4N BM anil	0.8N BM MSA	BM
1S	1/0	0.25 ml	-	1.25 ml
2S	1/1	0.25 ml	1.25 ml	-
3S	0/1	-	1.25 ml	0.25 ml

*** A/M stands for meq. of aniline/ meq. of MSA.

The FTIR spectra of these dilutions and the benzene-methanol mix spectrum are recorded in a FTIR spectrometer. The instrument used to record the spectra in this thesis is a FTS-7 from BIORAD, Digilab Division. The FTS-7 uses a Hughes HeNe laser operating in the VIS region at 632 nm. The detector (MCT) is maintained at 77^{o}K by a special cryogenic dewar filled with liquid N_2.

The SET UP spectrometer parameters are the following:

Detector:	internal
Scan speed:	5 kHz
Delay:	1.0 second
Low pass filter:	1.12 kHz
Collect sensitivity:	4

The SCAN parameters are the following:

Resolution:	4
No. Scans:	16
Start:	4000
End :	450

The background spectrum is recorded in single beam type and loaded into the computer memory. Once the solvent and the solutions spectra are recorded, the solute spectrum can be

acquired. The solute spectrum is obtained by subtracting the solvent spectrum from the solution spectrum.

Subtraction Technique

Each recorded spectrum (including solution and solvent spectrum), is converted by an operational function in the FTIR spectrometer. The signal obtained in transmittance is converted to absorbance. The subtraction is done (having solution and solvent an absorbance type of spectrum) by the subtraction operational function. At this point, the subtraction factor plays a role, dependent on the quantity of compound that can be subtracted. The subtraction factors are determined from the display field. The resulting subtracted spectra has an absorbance signal. It is required to make a conversion to transmittance signal. This spectrum is the final product of the subtraction technique.

The subtraction of solutions 1S, 2S, and 3S is displayed in three different spectra, one for each compound and the other for the mix which has new characteristics. Therefore, an interaction between aniline and methanesulfonic acid (MSA) takes place.

The interaction is then studied with 9 different ratios. The preparation of the original solutions is done with larger amounts than in the previous preparation. This time, 25 mL of 4N BM-75 solution of aniline and 100 mL of 0.8N BM-75 solution of MSA are needed. 9.3130 g and

7.6880 g are weighed respectively.

Nine dilutions (15 mL each) are prepared as follows:

	A/M	4N BM anil	0.8N BM MSA	BM
1.	1/0	2.5	-	12.5
2.	5/1	2.5	2.5	10.0
3.	2/1	2.5	6.25	6.25
4.	1.25/1	2.5	10.0	2.5
5.	1/1	2.5	12.5	-
6.	1/1.25	2.0	12.5	0.5
7.	1/2	1.25	12.5	1.25
8.	1/5	0.5	12.5	2.0
9.	0/1	-	12.5	2.5

Solutions 1 and 9 remain liquid. Solutions 2 through 8 are centrifuged for a period of 5-7 minutes each. The liquid portion is separated from the solid by decantation. The liquid portion is called top (T) and the solid, bottom (B). The extremes are called 1TB and 9TB. These and the 7 top solutions spectra are recorded two hours after their preparation. A drop of each solution is placed on the cell to obtain the spectra. The solvent (BM-75) spectrum is also recorded and then subtracted from each solution. The 7 bottom portions spectra are recorded by smearing a tiny solid portion on the minicell with a drop of benzene. The benzene was also subtracted from these spectra.

The subtraction factors that are utilized in the aniline : methanesulfonic acid interaction are the following:

ORIGINAL SPECTRUM	SUBTRACTION (Absorbance)	S.F.	FINAL SPECTRUM
1TB	1TBA-BMA	0.50	1TB-BM
2T	2TA-BMA	0.55	2T-BM
3T	3TA-BMA	0.55	3T-BM
4T	4TA-BMA	0.60	4T-BM
5T	5TA-BMA	0.60	5T-BM
6T	6TA-BMA	0.60	6T-BM
7T	7TA-BMA	0.70	7T-BM
8T	8TA-BMA	0.60	8T-BM
9TB	9TBA-BMA	0.70	9TB-BM
2B	2BA-BENZA	1.05	2B-BENZ
3B	3BA-BENZA	0.65	3B-BENZ
4B	4BA-BENZA	1.05	4B-BENZ
5B	5BA-BENZA	0.25	5B-BENZ
6B	6BA-BENZA	1.20	6B-BENZ
7B	7BA-BENZA	1.30	7B-BENZ
8B	8BA-BENZA	1.20	8B-BENZ

For the bottom portions spectra, the benzene added is variable in each combination. After the subtraction and regeneration to transmittance signal, the final subtracted spectrum is obtained for all of the samples. Finally, a complete analysis is thus performed.

Aniline : Phenyl Phosphinic Acid.

The 5.6836 g of phenyl phosphinic acid (FW 142.09) are accurately weighed and dissolved with BM-75 in a 50-mL volumetric flask to prepare a 0.8N BM-75 solution of phenyl phosphinic acid (PPA). To get 25 mL of 4N BM-75 solution of aniline (FW 93.13), 9.3130 g of aniline are precisely weighed and placed in a 25-mL volumetric flask.

Utilizing BM-75 as the solvent, nine dilutions (9 mL each) are made :

	A/P	4N BM anil	0.8 BM PPA	BM
AP1	1/0	1.5	-	7.5
AP2	5/1	1.5	1.5	6.0
AP3	2/1	1.5	3.75	3.75
AP4	1.25/1	1.5	6.0	1.5
AP5	1/1	1.5	7.5	-
AP6	1/1.25	1.2	7.5	0.3
AP7	1/2	0.75	7.5	0.75
AP8	1/5	0.3	7.5	1.2
AP9	0/1	-	7.5	1.5

*** A/P stands for meq. of aniline/ meq. of PPA.

As the solutions remain liquid, no further process follows. The spectra are recorded after 2 hours of preparation in an infrared minicell with AgBr windows positioned for smears. The subtraction is performed with those spectra and the benzene-methanol spectrum. The subtraction factors vary from 0.5 to 0.75, and the final spectrum is named AP#-BM (# depends on the solution). The final study for this interaction relies on the nine AP#-BM spectra.

Aniline : Benzoic Acid.

As in former studies, aniline is a 4N BM-75 solution. For the acid, 4.8848 g of benzoic acid (FW 122.12) are required to prepare 50 mL of a 0.8N BM-75 solution. The sample is accurately weighed and deposited in a 50-mL volumetric flask.

With these solutions and the solvent (BM-75), three dilutions are made (1.5 mL each):

	A/B	4N BM anil	0.8N BM Benzoic	BM
AB1	1/0	0.25	-	1.25
AB2	1/1	0.25	1.25	-
AB3	0/1	-	1.25	-

*** A/B stands for meq. of aniline/ meq. of benzoic acid.

The mix (1/1) remains liquid. The spectra are recorded after 2 hours of solution preparation. The subtraction is done with factors of 0.5, 0.6, and 0.3, respectively. The spectra are recorded once more after 24 hours of preparation with 0.6 as the common subtraction factor. The same results are obtained.

Phenol : Phenyl Phosphinic Acid.

Phenol (FW 94.11) in the amount of 0.7529 g, is accurately weighed and placed in a 10 mL volumetric flask to prepare a 0.8N BM-75 solution. As in earlier preparations, the sample was dissolved with benzene-methanol in a volume ratio 75/25 (prepared previously).

Phenyl phosphinic acid in the amount of 1.1367 g, is also precisely weighed and dissolved in BM-75 to prepare 10 mL of a 0.8N solution.

With these two 0.8N BM-75 solutions of phenol (Ph) and phenyl phosphinic acid (PPA), and benzene-methanol 75/25,

three dilutions (each containing 2.5 mL) are made. Ph/PPA stands for meq. of phenol/ meq. of PPA. The dilutions are the following:

	Ph/PPA	0.8N BM Ph	0.8N BM PPA	BM
PP1	1/0	1.25	-	1.25
PP2	1/1	1.25	1.25	-
PP3	0/1	-	1.25	1.25

The mix (1/1) continues to be a liquid. The spectra are recorded after 2 hours of preparation. Then, they are subtracted, and the interaction analysis is accomplished.

* FTIR Analysis of Polymers.

The FTIR analysis of polymers initiates studying the behavior of polymeric sulfonic acid, one of the two resins in this research. The analysis begins with its interaction with aniline, the first single compound selected to observe any spectrum modification when the polymer supported-reagent and a single compound such as aniline are placed together.

Aniline : Polymeric Sulfonic Acid.

The interaction takes place between 1 milliequivalent of aniline and 1 milliequivalent of polymeric sulfonic acid (according to model compound study "aniline : MSA").
The polymeric sulfonic acid beads that are synthesized in Dr. Alexandratos' laboratory and utilized for this study

have 4.18 meq OH^- / g of dry resin. In order to have 1 meq. of supported-reagent, 0.239 g of dry resin are needed.

The beads are always kept in distilled water to avoid collapsing. If they collapse, any interaction would be impossible. Therefore, the weight is based on buchner dry resin.

The polymeric sulfonic acid beads (buchner dry) for the test have 48.5% solids. Consequently, 0.4927 g of buchner dry resin are required to have 0.239 g of dry resin (1 meq.).

The polymeric sulfonic acid beads are buchner dry (usually 5 min.). The required amount, 0.4927 g is accurately weighed and placed in a vial with 10 mL of methanol. This is the first stage of the solvent exchange operation.

The solvent exchange is made 4 times with methanol and 4 times with benzene-methanol 75/25 mix. Each time, 10 mL of solvent are added and the solution is shaken for about 20 minutes. After the solvent exchange is done, the sample is set for the reaction with aniline.

To the polymer sample (1 meq.), 0.25 mL of 4N BM-75 solution of aniline and 10 mL of BM-75 are added. The vial is placed in a shaker overnight, for about 17 hours.

After the 17-hour period, the solvent is decanted, the vial is placed in a hood for 10 minutes, and then, it is taken to the oven (60^oC) overnight. When completely dry, a sample can be weighed to prepare a KBr pellet.

The polymer sample is 3% of a total of 0.150 g of solid to make the pellet. The solid (0.0045 g of sample + KBr) is ground for 3 minutes and then pressed for 7 minutes to form the pellet: 1 minute and 8,000 lb/in^2 with the cell in one direction and 6 minutes and 16,000 lb/in^2 with the cell in the opposite direction to seek for a uniform pellet. The spectrum is recorded with the KBr-pellet cell.

To compare the mix, the aniline spectrum is recalled from the aniline : benzoic acid interaction. The polymeric sulfonic acid beads are dried after the solvent exchange to get a KBr pellet. The same steps are followed. After completely dry, the beads are weighed (3% in a 0.150 g KBr pellet), ground and pressed. With the pellet, the spectrum is recorded.

The interaction is analyzed by comparing the three spectra: aniline, polymeric sulfonic acid, and mix (1:1).

Aniline : Polymeric Phosphinic Acid.

According to the aniline : phenyl phosphinic acid interaction, the interaction between aniline and polymeric phosphinic acid takes place from milliequivalent (meq.) to milliequivalent.

The polymeric phosphinic acid beads synthesized in Dr. Alexandratos' laboratory and used for this test, have 5.15 meq. OH^- / g of dry phosphinic resin. In order to

have 1 milliequivalent of supported reagent, 0.19417 g of dry resin are necessary. The resin (buchner dry) has 50% solids; therefore, 0.3883 g of buchner dry resin have to be weighed.

The steps carried out with polymeric phosphinic acid are the same as those carried out with polymeric sulfonic acid. The solvent exchange is done 4 times with methanol and 4 times with benzene-methanol (20 minutes shaking each). This process is performed for two samples. The first sample, the single compound sample, is taken to the hood and then to the oven. The second sample of resin is placed with 0.25 mL of a 4N BM-75 solution of aniline to interact in a shaker for about 17 hours. This is the mix sample. The aniline spectrum is recalled from the aniline : benzoic acid interaction.

The pellet is made, as earlier, with 3% of sample for a total of 0.150 g with KBr. The powder is ground, and taken to the cell. Then, it is pressed and the spectrum is recorded.

To run the solid samples in the FTIR spectrometer, the KBr pellet without sample serves as a background. The background spectra are run in a single beam signal instead of utilizing a transmittance signal.

* <u>FTIR Analysis of Substituted Anilines/ Model Compounds</u>.

This investigation compares the effect of a proton

donor group has on the benzene ring and the effect of an electron withdrawer group has on the same ring. The substituent effect is thus analyzed by FTIR.

p-Methoxyaniline : Methanesulfonic Acid.

For this analysis, a 1N BM-75 solution of p-methoxyaniline (PMA) and a 0.8N BM-75 solution of MSA are used. 1.2316 g are accurately weighed to prepare 10 mL of a 1N BM-75 solution of p-methoxyaniline (FW 123.16). They are placed in a 10-mL volumetric flask and dissolved with benzene-methanol 75/25 prepared previously.
For the preparation of a 0.8N BM-75 solution of MSA, see "Aniline : Methanesulfonic acid", the interaction studied at the beginning of this chapter.
With these two solutions and the solvent, three dilutions (2.25 mL each) are prepared:

	PMA/MSA	1N BM PMA	0.8N BM MSA	BM
PMMS1	1/0	1	-	1.25
PMMS2	1/1	1	1.25	-
PMMS3	0/1	-	1.25	1

The spectra are recorded 3 hours after the preparation of the dilutions. The solvent is then subtracted. The subtraction factors are 0.6 for PMMS1, 1.0 for PMMS2, and 0.7 for PMMS3. The analysis is carried out with the subtracted spectra.

m-Chloroaniline : Methanesulfonic acid.

Besides the 0.8N BM-75 solution of methanesulfonic acid, a 4N BM-75 solution of m-chloroaniline (MCA) is required to perform this analysis.

m-Chloroaniline (FW 127.57), 5.1028 g , is accurately weighed, placed in a 10-mL volumetric flask, and dissolved with BM-75 to make a 4N BM-75 solution of m-chloroaniline. As in former interactions, three dilutions (2 mL each) are made with BM-75:

	MCA/MSA	4N BM MCA	0.8N BM MSA	BM
MCMS1	1/0	0.25	-	1.75
MCMS2	1/1	0.25	1.25	0.50
MCMS3	0/1	-	1.25	0.75

The spectra are run 3 hours after the preparation of the dilutions. The subtraction factors are 0.7 for MCMS1, 0.7 for MCMS2, and 0.6 for MCMS3. The analysis is performed with the subtracted spectra.

p-Methoxyaniline : Phenyl phosphinic acid.

This study is worked with a 1N BM-75 solution of p-methoxyaniline and a 0.8N BM-75 solution of phenyl phosphinic acid. For the preparation of p-methoxyaniline solution see "p-Methoxyaniline : methanesulfonic acid". For the preparation of phenyl phosphinic acid solution, see Phenol : Phenyl phosphinic acid".

Three dilutions (each containing 2.25 mL) are prepared as follows:

	PMA/PPA	1N BM PMA	0.8N BM PPA	BM
PMPP1	1/0	1	-	1.25
PMPP2	1/1	1	1.25	-
PMPP3	0/1	-	1.25	1

The spectra are run 3 hours after the preparation of the solutions. The subtraction factors are 0.5 for PMPP1, 0.7 for PMPP2, and 0.7 for PMPP3. The investigation is done with the subtracted spectra obtained from the experiment.

m-Chloroaniline : Phenyl phosphinic acid.

The solutions required for this study are a 4N BM-75 solution of m-chloroaniline and a 0.8N BM-75 solution of phenyl phosphinic acid. Their preparation can be seen under "m-Chloroaniline : Methanesulfonic acid" and under "Phenol: Phenyl phosphinic acid" respectively.

Three dilutions (1.5 mL each) are made:

	MCA/PPA	4N BM MCA	0.8N BM PPA	BM
MCPP1	1/0	0.25	-	1.25
MCPP2	1/1	0.25	1.25	-
MCPP3	0/1	-	1.25	0.25

The solutions spectra are run after 3 hours of preparation. The subtraction factors are 0.35 for MCPP1, 0.6 for MCPP2,

and 0.6 for MCPP3. The study with model compounds and substituted anilines are thus concluded after this spectra analysis.

* FTIR Analysis of Substituted Anilines/ Polymer-Supported Reagents.

The substituent effect is investigated with polymer-supported reagents to analyze the differences presented on the interactions when the substituent group is changed on the benzene ring of aniline.

p-Methoxyaniline : Polymeric sulfonic acid.

The interaction is analyzed by taking a 1N BM-75 solution of p-methoxyaniline and 1 milliequivalent of polymeric sulfonic acid.

As in former interactions with aniline, 1 meq. of polymeric sulfonic acid corresponds to 0.4927 g of buchner dry resin. The solvent exchange is performed with methanol and benzene-methanol (75/25). To the vial with the resin beads, 1 mL of 1N BM-75 solution of p-methoxyaniline is added. The preparation of this solution appears under "p-Methoxyaniline : Methanesulfonic acid". Benzene-methanol (75/25) is also added in the amount of 9 mL, and the vial is left overnight (17-hours reaction) in a shaker.

After the period of contact, the solvent is decanted. The vial is then placed in a hood for 5 minutes, and then

dried at 60°C in the oven. Two samples are taken to make the KBr pellet: the first sample is dried for 3 hours; the second sample is dried for 24 hours. The same spectrum is obtained.

The pellet has a total weight of 0.120 g . The sample makes up only 2.5% of this weight, and KBr is the remaining weight. The powder is ground for 3-5 minutes and pressed for 5-7 minutes. The mix is called SUlfonic-PMA (SUPMA). For this analysis, the two single spectra are taken from former interactions.

m-Chloroaniline : Polymeric sulfonic acid.

To work and analyze this interaction, 1 milliequivalent of polymeric sulfonic acid (0.4927 g of buchner dry resin) and 0.25 mL of 4N BM-75 solution of m-chloroaniline are required.

The same steps as in the interaction studied before are followed. After the solvent exchange, 1 meq. of each compound and 9.75 mL of BM-75 are placed in a vial. After reaction, the mix is dried and, as before, the two samples (3h and 24h dry) provide the same results. The pellet is made with the same procedure. From a total weight of 0.120 g of KBr pellet, the sample is 2.5% and the remainder is KBr. The powder was also ground for about 3-5 minutes and pressed for 5-7 minutes in a laboratory press. The mix spectrum is called SUlfonic-MCA (SUMCA). The spectra for

m-chloroaniline and the polymeric sulfonic acid are taken from former interactions to compare with the mix and to complete the interaction analysis.

p-Methoxyaniline : Polymeric phosphinic acid.

For this analysis, 1 milliequivalent of polymeric phosphinic acid is required, as well as 1N BM-75 solution of p-methoxyaniline.

In this case, 1 meq. of polymeric phosphinic acid corresponds to 0.3883 g of buchner dry resin. For the reaction initiation, 1 mL of 1N BM-75 solution of p-methoxyaniline and 9 mL of BM-75 are added to the vial with the resin. The same steps (see p-methoxyaniline : polymeric sulfonic acid) are followed after the reaction.

After making the KBr pellet, the spectrum is run in the FTIR spectrometer. The mix spectrum is called PHosphinic-PMA (PHPMA). The analysis is accomplished by taking this spectrum and the two others (P-methoxyaniline and polymeric phosphinic acid) from former interactions.

m-Chloroaniline : Polymeric phosphinic acid.

To a meq. of polymeric phosphinic acid (0.3883 g buchner dry resin) placed in a vial, 0.25 mL of a 4N BM-75 solution of m-chloroaniline and 9.75 mL of BM-75 are added to initiate the reaction.

The solution is left overnight for about 17 hours.

The same steps follow, as in former interactions. After the dry process, the KBr pellet is formed, and the spectrum is run. The mix spectrum is named PHosphinic-MCA (PHMCA).

The interaction analysis is concluded by analyzing this spectrum and the others (each compound by itself) from former interactions.

All recorded spectrum requires a recorded background in the FTIR spectrometer. For liquid samples, the background is the spectrum of the minicell without the sample. For the solid samples, the background is the spectrum of a KBr pellet with no sample. The background is subtracted automatically by the equipment.

*Strength of Intermolecular Hydrogen Bond (solid/solution)

Benzoic acid.

This study is carried out to compare the bonds that appear in a solid sample of benzoic acid and in a BM-75 solution of this acid with the bond that appears in the subtracted spectrum of benzoic acid from this BM-75 solution.

The solid benzoic acid is studied by making a KBr pellet and running the spectrum. Two samples are prepared: The first, a KBr pellet with 0.120 g and benzoic acid in an amount of 1%. The second, a KBr pellet with 0.120 g and benzoic acid in an amount of 0.5%. The best spectrum is obtained with the second sample.

The benzoic acid solution is analyzed by taking its

spectrum from the aniline : benzoic acid interaction. The spectrum corresponds to the solution with a 0/1 ratio or 1 meq. of benzoic acid / 1.5 mL total solution.

The subtracted spectrum is obtained by subtracting the solvent from the solution spectrum with 0.6 as the subtraction factor (S.F.). Another subtraction is made to this subtracted spectrum, to remove more solvent. The S.F. is 0.15 for the second subtraction. Inverted peaks are obtained by increasing the factor to 0.2; the double subtracted factor is used for the comparison.

Phenyl phosphinic acid (PPA).

This investigation was performed, not only to compare the bond in the solid compound with the dissolved compound, but also to contrast the link with the benzoic acid bond.

The solid PPA spectrum is obtained with a KBr pellet. The pellet has 0.120 g and 0.6% of this weight is from phenyl phosphinic acid.

The solution spectrum is taken from the aniline : PPA interaction and the subtracted spectrum to conclude this study.

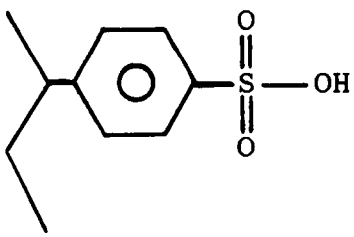
CHAPTER IV

MOLECULAR RECOGNITION MECHANISMS

The interaction displayed by polymer-supported reagents through model compound studies is central to this section. Polymeric sulfonic acid and polymeric phosphinic acid are the resins in this research. Model compounds include methanesulfonic acid, phenyl phosphinic acid, and benzoic acid. Aniline and aniline derivatives were chosen to interact with model compounds and resins.

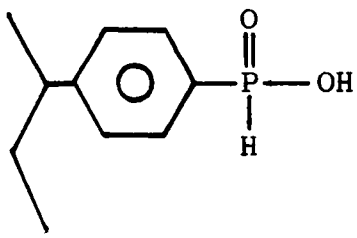
This model compound study will serve as a basis to understand the behavior of polymer-supported reagents' interaction with molecules. The interaction of polymer-supported reagents with aniline, para-methoxyaniline, and meta-chloroaniline is thus studied by Fourier Transform Infrared (FTIR) analysis.

The structures of these compounds are the following:



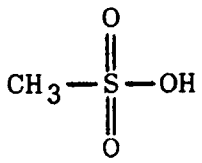
Polymeric sulfonic acid

(SULFONIC RESIN)

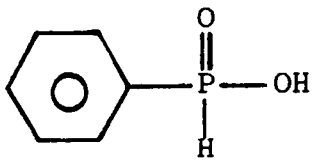


Polymeric phosphinic acid

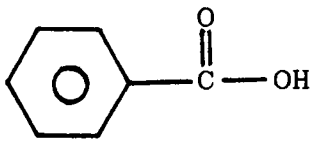
(PHOSPHINIC RESIN)



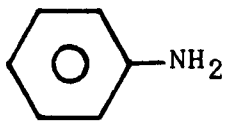
Methanesulfonic acid



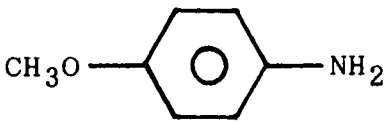
Phenyl phosphinic acid



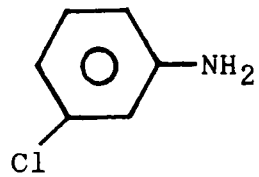
Benzoic acid



Aniline



p-Methoxyaniline



m-Chloroaniline

* Previous Infrared Studies.

Initially, methanesulfonic acid and aniline were investigated by infrared (IR) analysis to find any interaction between them.

Three spectra were recorded in an infrared spectrometer:

1) Methanesulfonic acid, 0.2N methanol solution

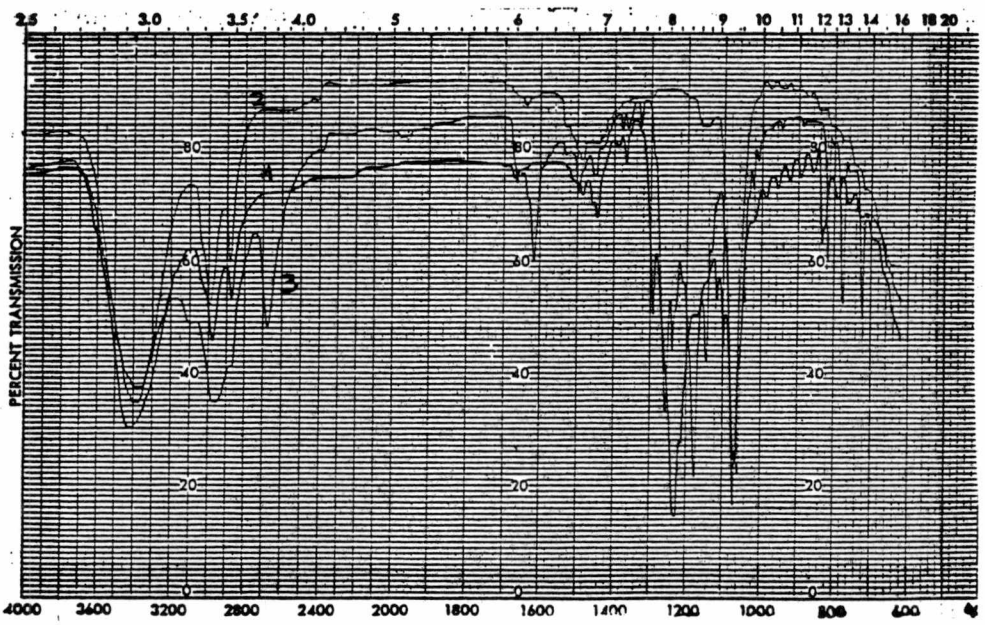
2) Aniline, 0.2N methanol solution

3) Mix, 1 milliequivalent (meq.) each, of 1 and 2

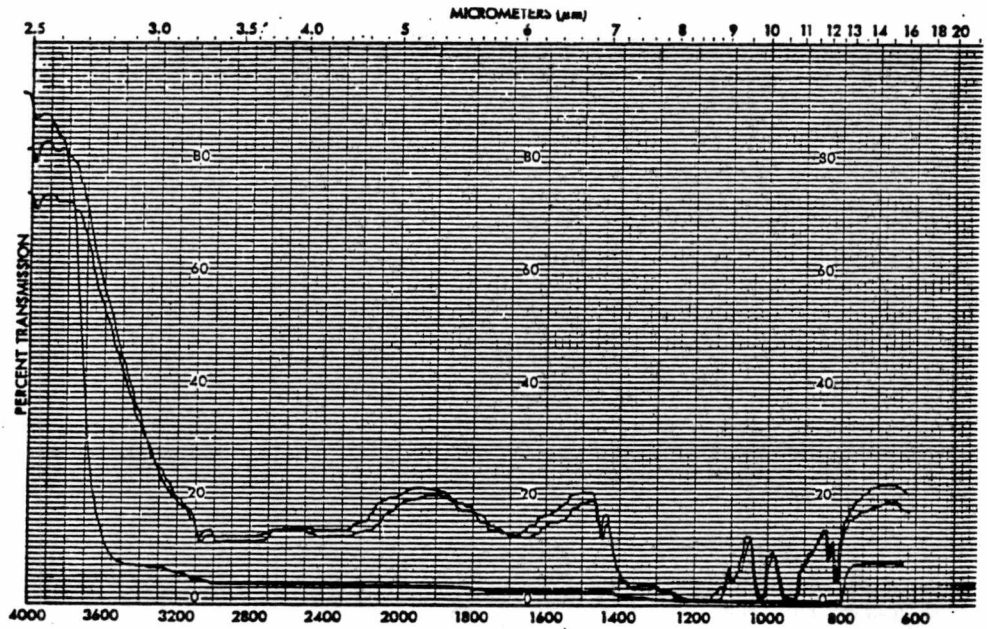
(IR spectrum 1 - Figure 1).

The various IR spectra are shown in figure 1.

The mix (1:1) of these two compounds is a liquid and

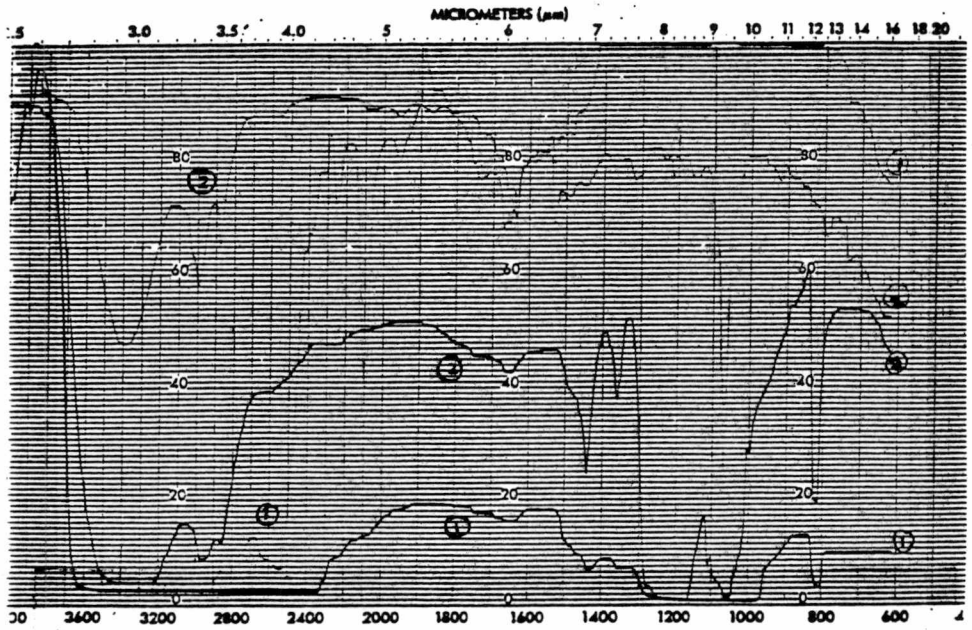


IR spectrum 1. Multispectral display: study in methanol. (1) MSA, solution 0.2N, (2) Aniline, solution 0.2N, and (3) Mix (1 meq. of each compound).

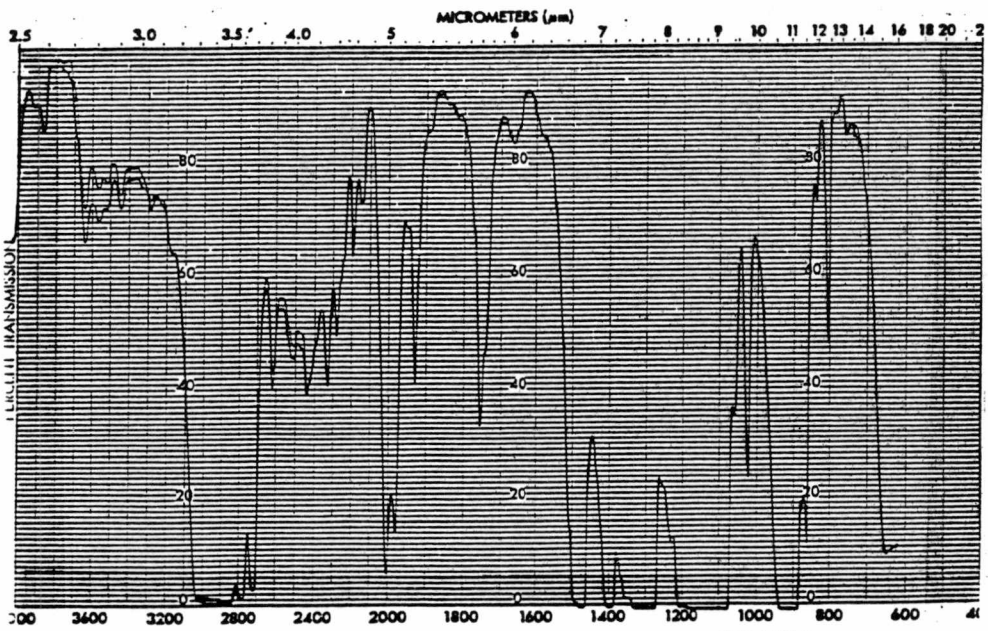


IR spectrum 2. Pure methanesulfonic acid (MSA). A tiny drop was placed in the cell and the spectrum was recorded three times consecutively.

FIGURE 1. IR spectra 1-6 and FTIR 1

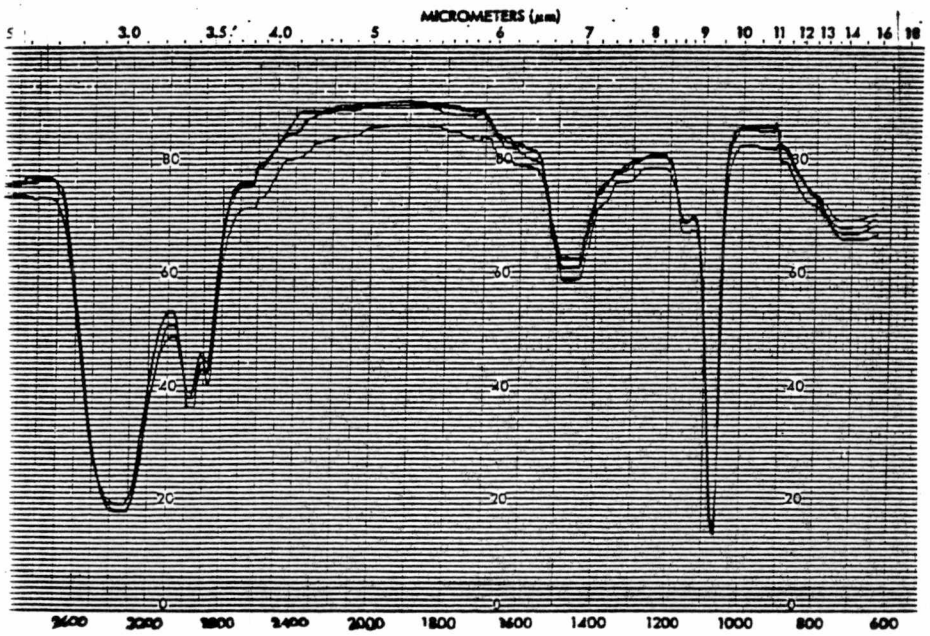


IR spectrum 3. Aniline / MSA / Solvent: methanol. 1N methanol solutions of aniline and MSA recorded twice consecutively.

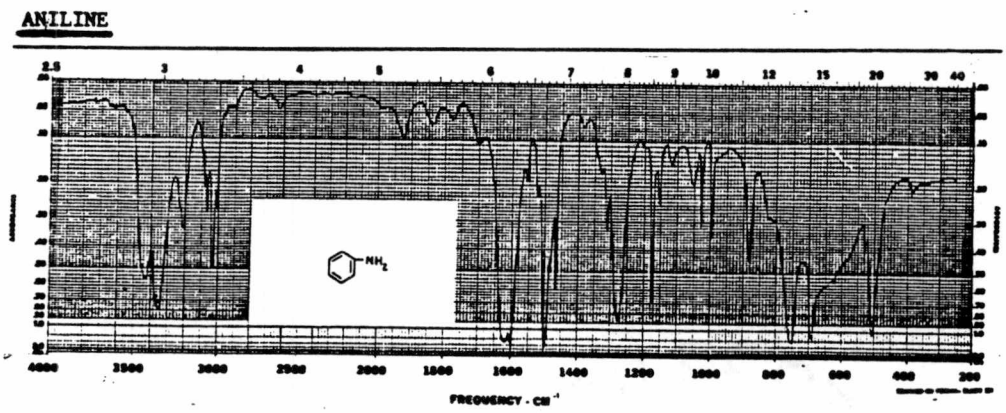


IR spectrum 4. MSA in dioxane. A 0.2N solution of methanesulfonic acid recorded twice continually.

FIGURE 1. (Continued)



IR spectrum 5. Aniline in methanol. A 0.2N methanol solution of aniline recorded four times consecutively.



IR spectrum 6. Standard aniline (Sadtler).

FIGURE 1. (Continued)

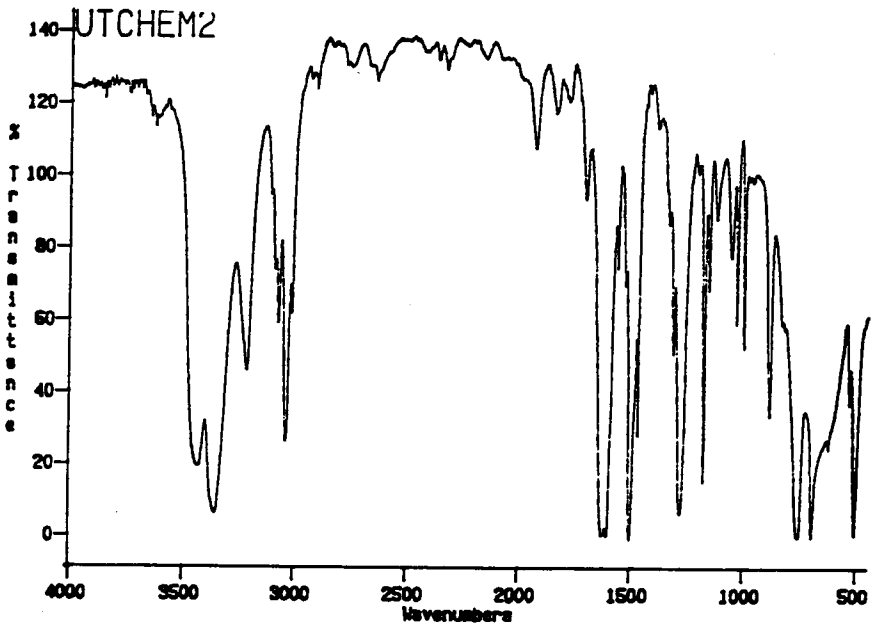


FIGURE 1. (Continued). FTIR 1. Pure aniline. This spectrum was experimentally obtained by placing a drop of the pure compound in the minicell.

yields a new, strong peak at about 2600 cm^{-1} in the IR spectrum 1 (3). Methanol makes the spectral differences hard to interpret due to its strong infrared absorption. When the concentrations of the solutions are increased to 1N, the mix (1:1) produces very shiny, white crystals.

The IR cell used has a rectangular mounting with NaCl windows. Every time it is utilized, a white film forms, impeding the light beam passing through the sample. There is probably an interaction between the NaCl of the cell window and methanol, the common solvent for all the solutions.

For pure compounds, the aniline spectrum can be obtained easily. On the contrary, it is really difficult to get an acceptable spectrum for methanesulfonic acid (IR spectrum 2 - Figure 1).

There is also no reproducibility when methanol is used as the solvent and the sample is placed in a cell with NaCl windows. The second time the test was recorded, the spectra yielded peaks at smaller absorbances. In the IR spectrum 3 (Figure 1), 1N methanol solutions of aniline and methanesulfonic acid were recorded twice consecutively.

Working with dioxane as the common solvent, reproducibility is obtained, but dioxane has many absorption bands that make the differentiation even more difficult. In the IR spectrum 4 (Figure 1), a 0.2N dioxane solution of methanesulfonic acid has been recorded twice continually.

* Choice of cell for FTIR studies.

Although they are expensive, AgBr windows are used in IR cells with reliable results. By using a minicell with AgBr windows, reproducibility is obtained for the compounds dissolved in methanol. IR spectrum 5 (Figure 1) shows a 0.2N methanol solution of aniline recorded four times consecutively.

For the present study, a minicell with AgBr windows positioned for smears (flat-flat surface) is used for a liquid or suspension sample. In the case of solid samples, polymers and polymer-single compound mixes, a KBr-pellet cell is utilized.

* Choice of solvent with Aniline as Standard Compound.

There is no IR or UV standard spectra in the literature for methanesulfonic acid. There is, however, a nuclear magnetic resonance spectrum (Sadtler).

The spectrum could be obtained by recording the FTIR spectrum of methanesulfonic acid in solution and then subtracting the solvent spectrum. In order to have a subtracted spectrum, aniline (Sadtler IR spectrum 6 and experimentally obtained FTIR 1 - Figure 1) is dissolved in the same solvents that methanesulfonic acid is dissolved. To have the best spectrum for aniline by solvent subtraction (similar to the standard spectrum) means to have, at the same time, a "standard" spectrum for methanesulfonic

acid (by subtracting the same solvent).

Methanol was the first solvent used. Methanesulfonic acid and aniline are soluble but the subtracted aniline spectrum (aniline spectrum by solvent subtraction) does not look like the standard because of the strong IR absorption of methanol (Figure 2). The subtraction factor (S.F.) was 1.0 in figure 2. When the factor is decreased to 0.7 (Figure 3), a better baseline is obtained. Subtraction was also done with 1.5 (Figure 4). None of the factors provides the expected results.

Ethanol gives a better spectrum (Figure 5). The subtraction factor is 1.0, but it does not approach to the standard aniline. A closer spectrum to the standard (Figure 6) is obtained with acetone (S.F.= 0.1), but this solvent is oxidized by methanesulfonic acid.

Cyclohexane has a clean IR spectrum and could be used as a solvent, but aniline is insoluble in cyclohexane. Carbon tetrachloride has a cleaner spectrum (above in Figure 7). A 1N carbon tetrachloride solution of aniline is also recorded (below), but methanesulfonic acid does not dissolve in carbon tetrachloride.

As solvents, petroleum ether and chloroform do not yield the subtracted aniline standard spectrum either. Aniline is partially soluble in petroleum ether. Figure 8 shows a subtracted aniline spectrum, which was obtained by subtracting the spectrum of petroleum ether (pure) from the

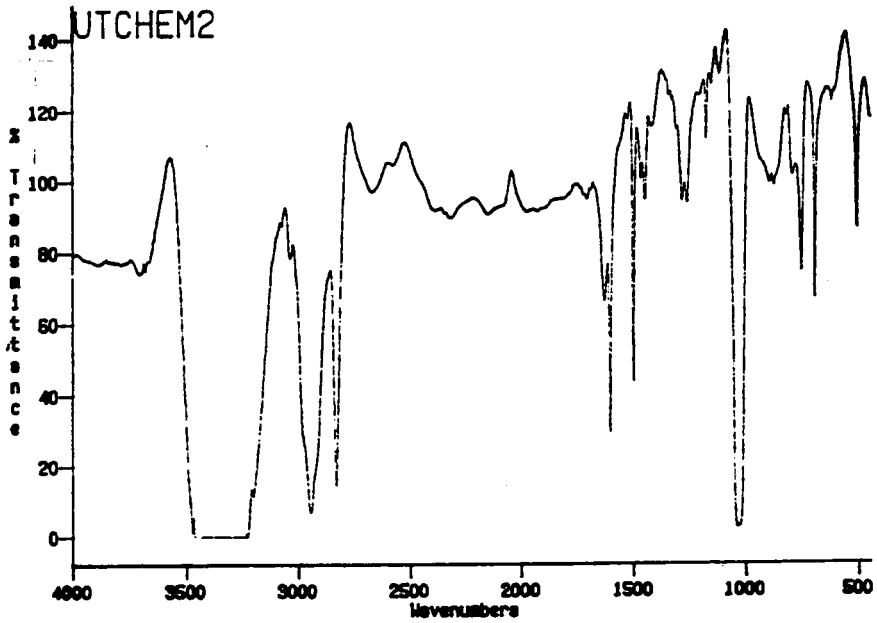


FIGURE 2. FTIR 2. Subtracted aniline (S.F.= 1.0). Aniline spectrum after methanol subtraction from a 1N methanol solution of aniline.

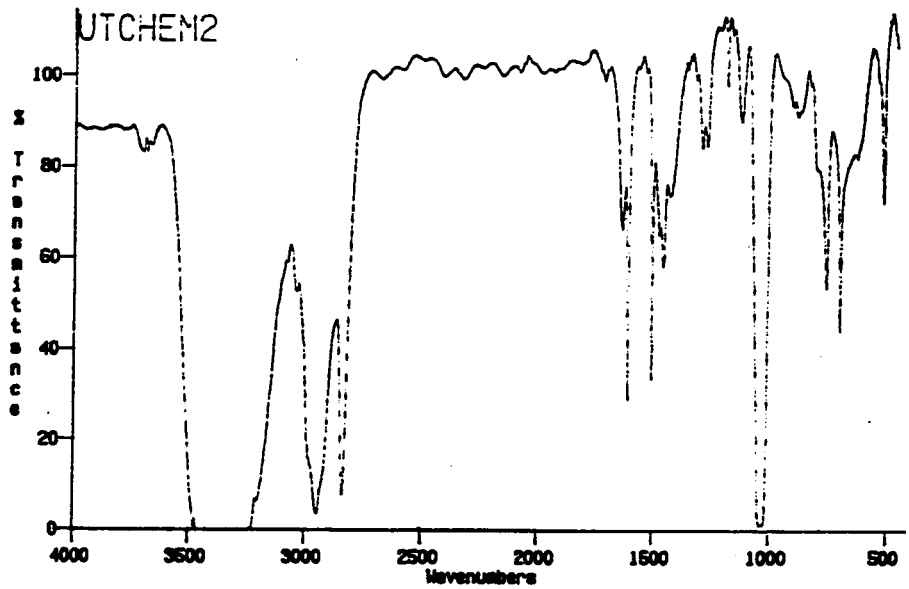


FIGURE 3. FTIR 3. Subtracted aniline (S.F.= 0.7). Aniline spectrum after methanol subtraction from a 1N methanol solution of aniline.

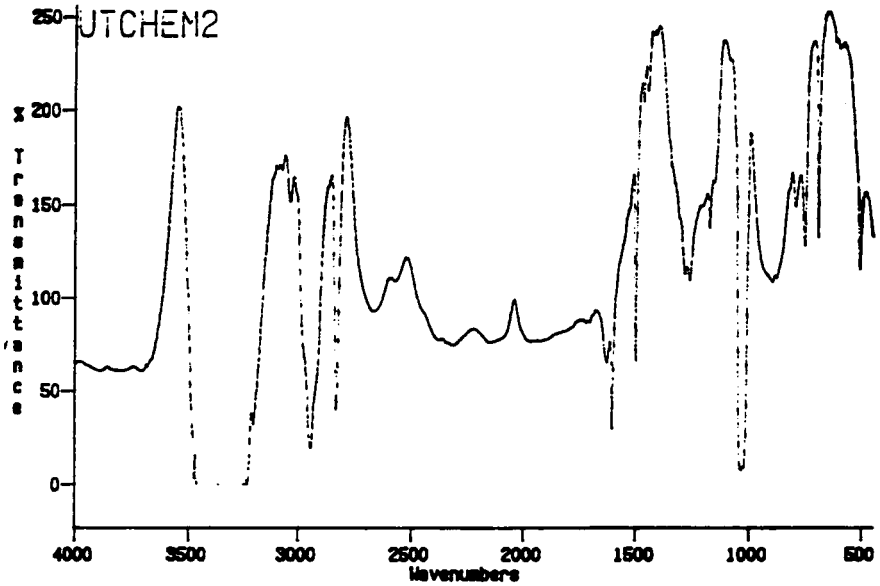


FIGURE 4. FTIR 4. Subtracted aniline (S.F.= 1.5). Aniline spectrum after methanol subtraction from a 1N methanol solution of aniline.

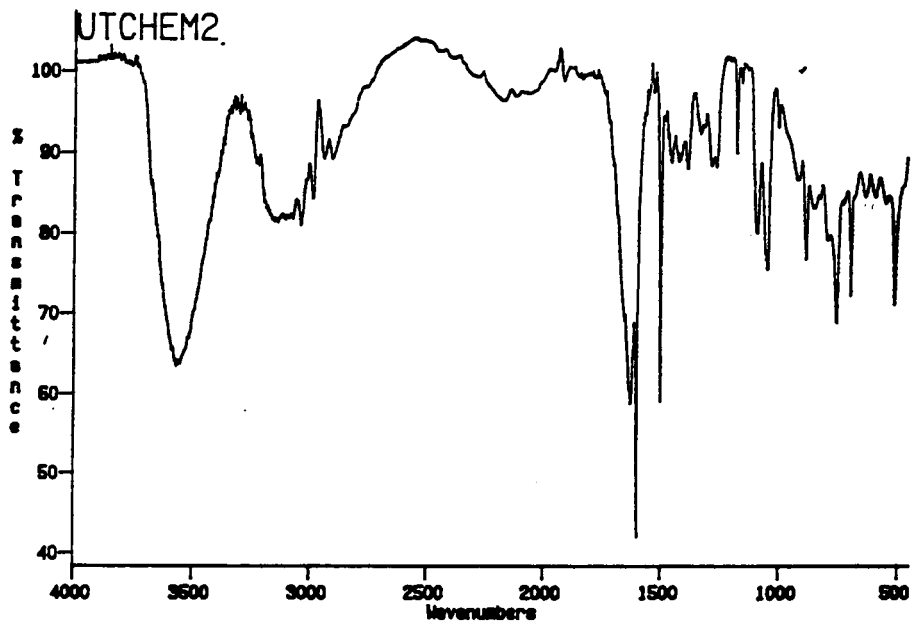


FIGURE 5. FTIR 5. Subtracted aniline (Ethanol). Aniline spectrum after ethanol subtraction from a 0.5N ethanol solution of aniline (S.F.= 1.0).

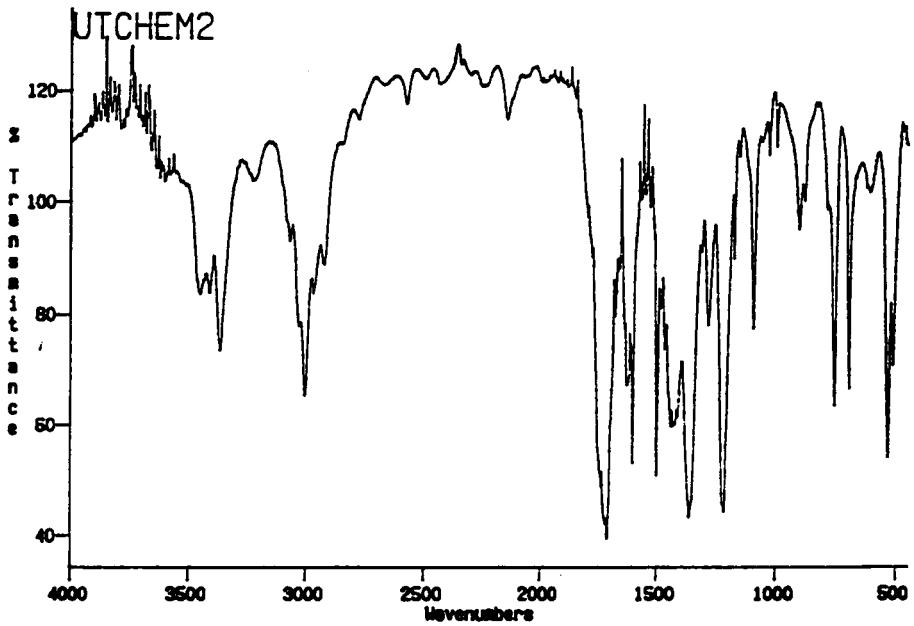


FIGURE 6. FTIR 6. Subtracted aniline (Acetone). Aniline spectrum after acetone subtraction from a 0.5N acetone solution of aniline (S.F.= 0.1).

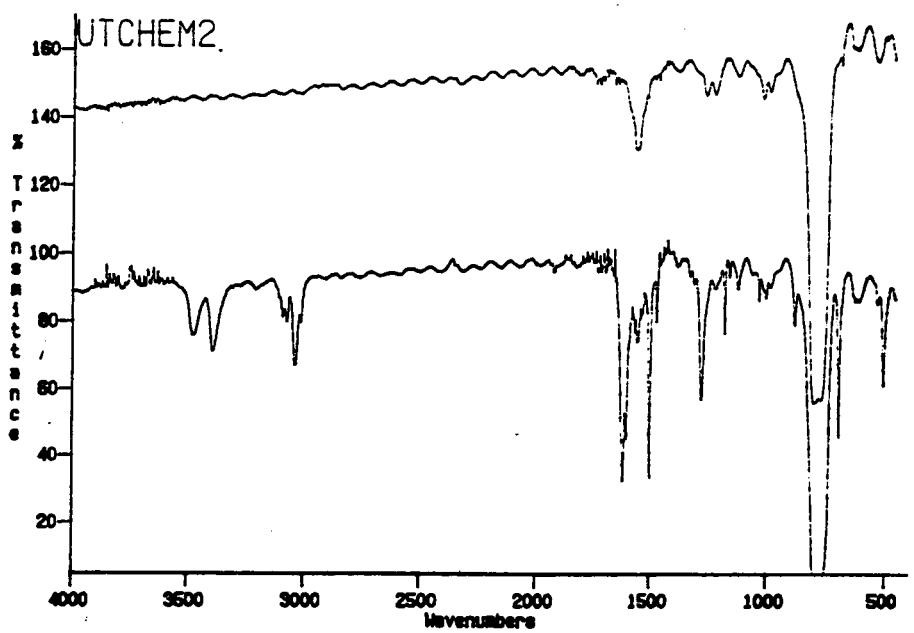


FIGURE 7. FTIR 7. Carbon tetrachloride/ 1N CCl_4 solution of aniline. The pure solvent is shown above. The solution is recorded below.

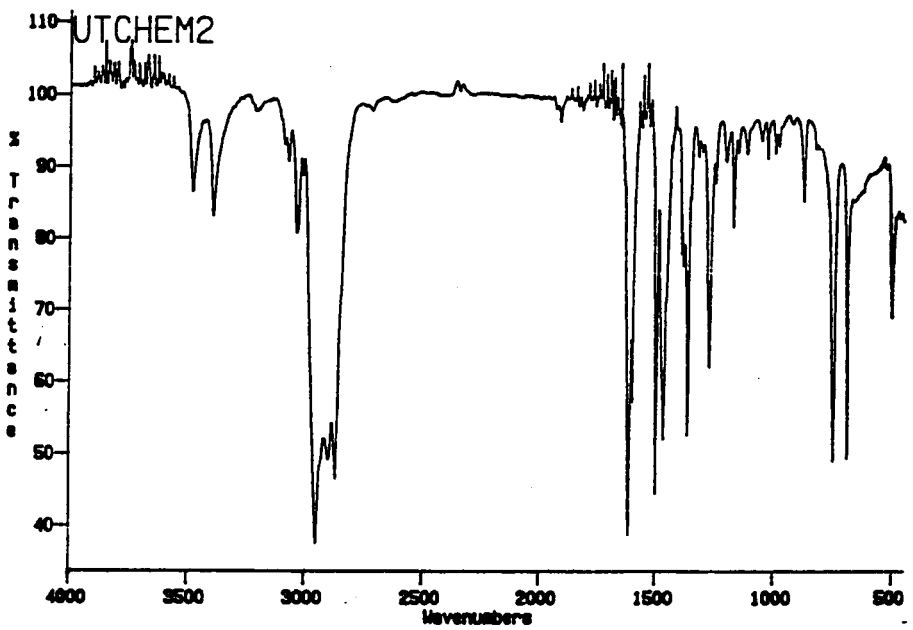


FIGURE 8. FTIR 8. Subtracted aniline (Petroleum ether). Aniline spectrum after petroleum ether subtraction from a 0.5N petroleum ether solution of aniline (S.F.= 1.0).

spectrum of 0.5N petroleum ether solution of aniline. Although subtracted, the strong band at about 2900 cm^{-1} comes from the solvent. Regarding chloroform, Figure 9 displays the aniline spectrum obtained from the subtraction of the spectrum of chloroform from the spectrum of 0.5N chloroform solution of aniline. In Figure 10, three spectra were recorded:

1) Aniline, 1.2N chloroform solution (above)
2) Methanesulfonic acid, 0.4N chloroform solution (below)
3) Mix (1:1) of 1 and 2 (middle). This forms a new peak at about 2600 cm^{-1}, as seen in previous infrared studies.

The subtraction of the chloroform from each of these three spectra does not make any difference.

Working with dioxane, as noted before, is difficult. Both aniline and methanesulfonic acid are soluble in this solvent, but dioxane does not have a clean spectrum, making the subtraction very hard.

The solvent study was also worked with isopropyl alcohol, and the results were similar to the alcohols studied before. Figure 11 exposes the subtraction of the isopropyl alcohol spectrum (S.F.= 1.0) from a 0.5N solution of aniline. Figure 12 gives the subtraction of this solvent spectrum (S.F.= 0.55) from a 0.2N solution of methanesulfonic acid. Finally, Figure 13 exhibits the subtraction of the solvent spectrum (S.F.= 0.8) from a mix (2 mL each).

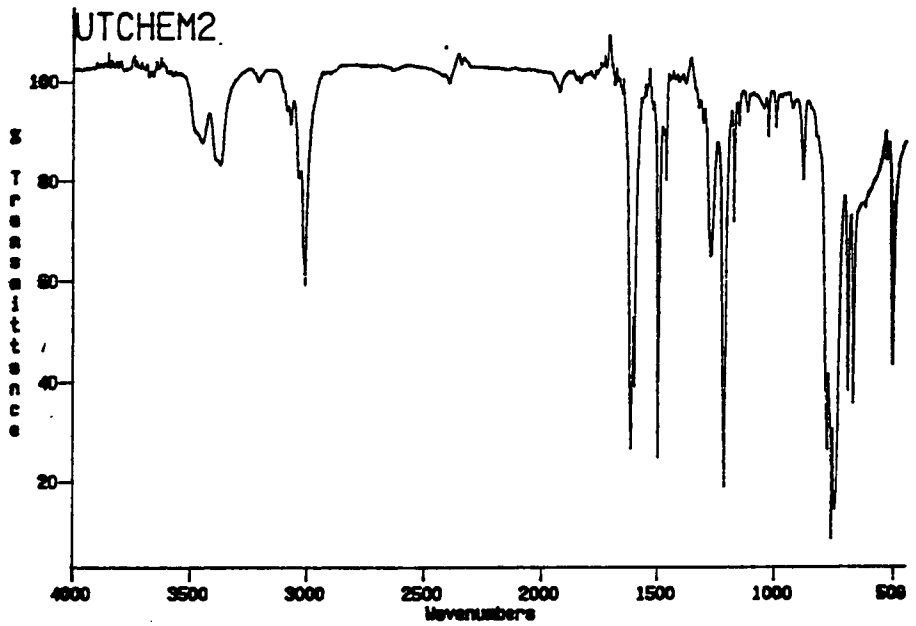


FIGURE 9. FTIR 9. Subtracted aniline (Chloroform). Aniline spectrum after chloroform subtraction from a 0.5N chloroform solution of aniline (S.F.= 1.0).

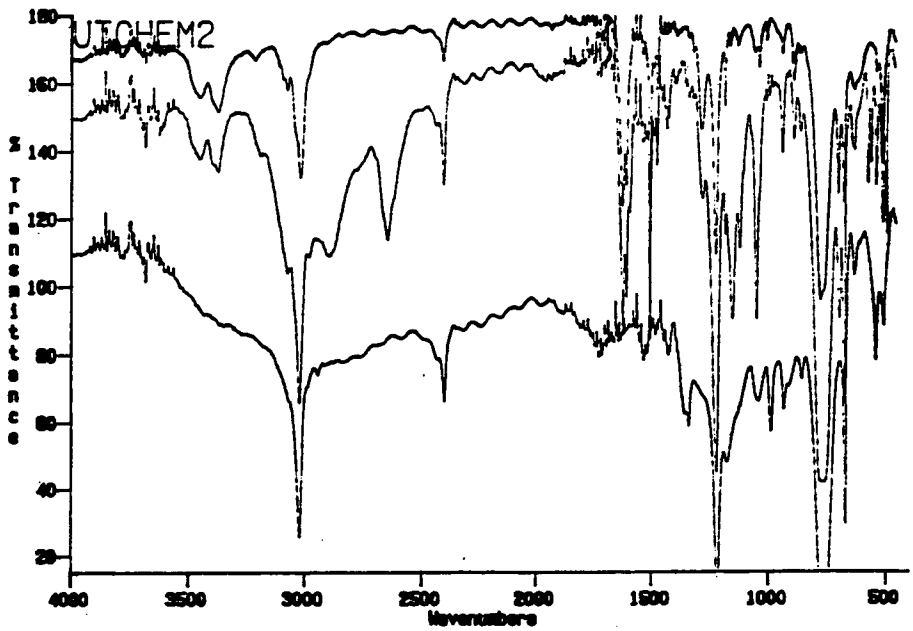


FIGURE 10. FTIR 10. Multispectral display: aniline/ MSA/ mix (1:1). A 1.2N chloroform solution of aniline is shown above, a 0.4N chloroform solution of MSA is shown below, and the mix is the spectrum in the middle.

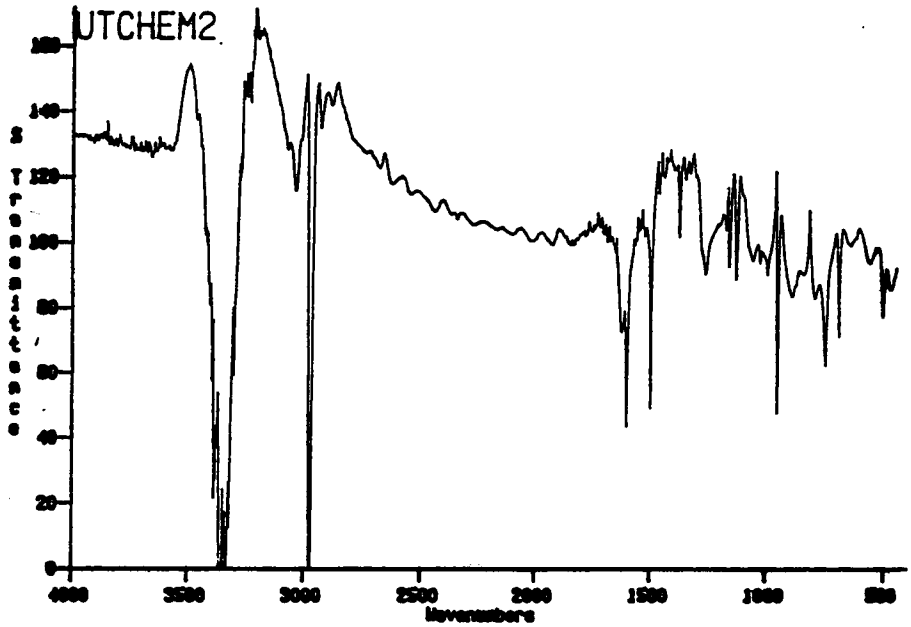


FIGURE 11. FTIR 11. Subtracted aniline (Isopropyl alcohol). Aniline spectrum after isopropyl alcohol subtraction from a 0.5N alcoholic solution of aniline (S.F.= 1.0).

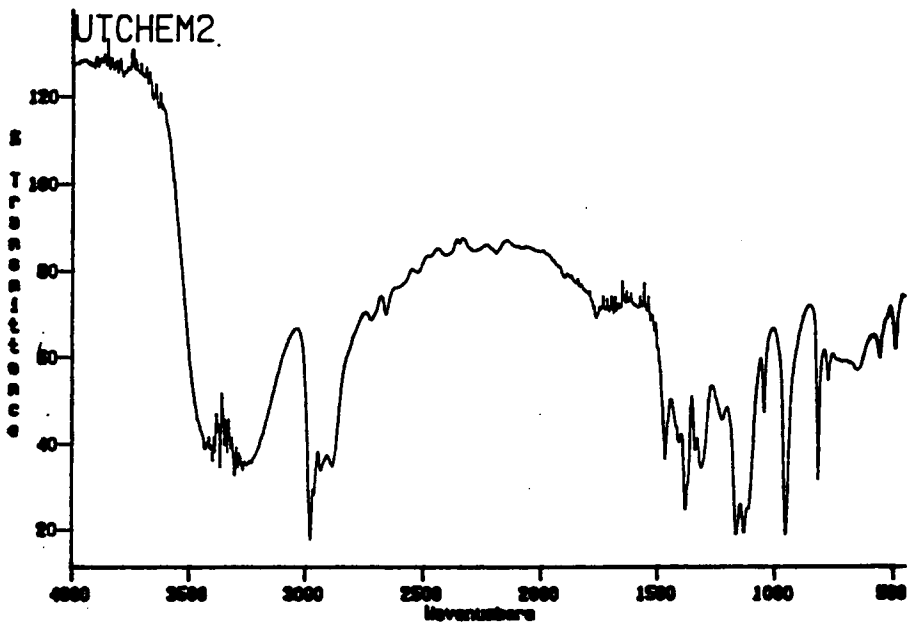


FIGURE 12. FTIR 12. Subtracted MSA or methanesulfonic acid (Isopropyl alcohol). MSA spectrum after isopropyl alcohol subtraction from a 0.2N alcoholic solution of MSA (S.F.= 0.55).

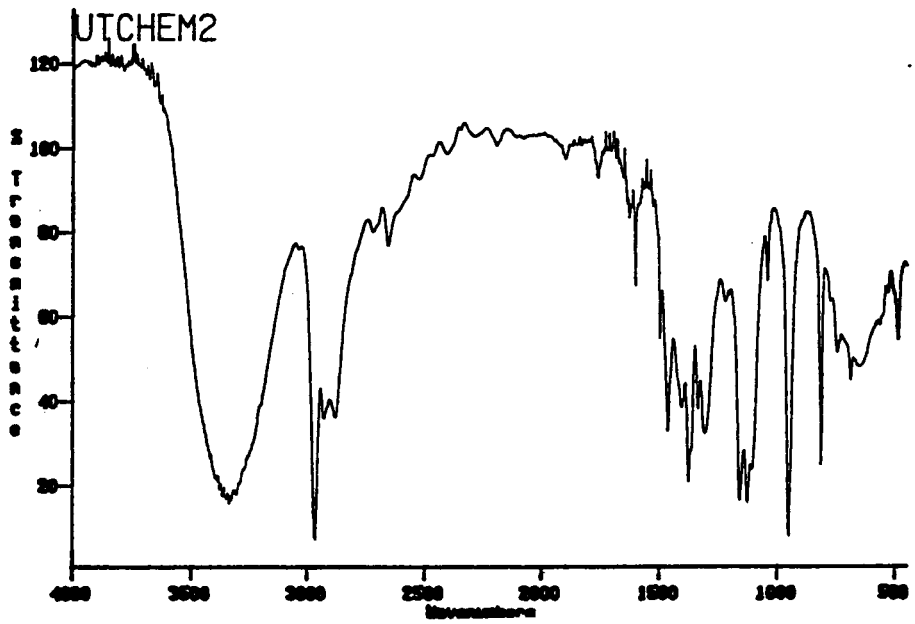


FIGURE 13. FTIR 13. Subtracted mix (Isopropyl alcohol). Mix spectrum (2 mL of 0.5N isopropyl alcohol solution of aniline and 2 mL of 0.2N isopropyl alcohol solution of MSA) after solvent subtraction (S.F.= 0.8).

In terms of subtraction, benzene could be a good solvent for aniline. As a polar compound, methanesulfonic acid has to be dissolved in a polar compound. Therefore, a mix of solvents could be an alternative to using a single solvent.

Using methanol in a low concentration is a possible alternative to working with subtraction problems. Benzene-methanol in a volume ratio 90/10 was the first attempt to get reliable spectra for aniline and methanesulfonic acid, but the latter compound is not soluble at that ratio.

Working with benzene-methanol (85/15) as the solvent and 1.2N solution of aniline, 0.4N solution of methanesulfonic acid, and a mix of 2 mL of each compound, the following results were obtained:

Figure 14 displays the benzene-methanol (85/15) mix. The abbreviation for the solvent mix in this text will be BM, and the number will be the percentage of benzene in volume; consequently, this solvent will be named BM-85. In the spectrum, the O-H stretching frequency at 3300 cm^{-1} is not as strong as it was with methanol and ethanol. Figure 15 exhibits a 1.2N BM-85 solution of aniline. It is possible to observe a difference in that frequency due to the N-H stretching that was not possible when methanol was used as a solvent. Figure 16 shows the 0.4N BM-85 solution of methanesulfonic acid, and Figure 17 displays the spectrum of the two-compound mix, in which a new peak at about 2600 cm^{-1}

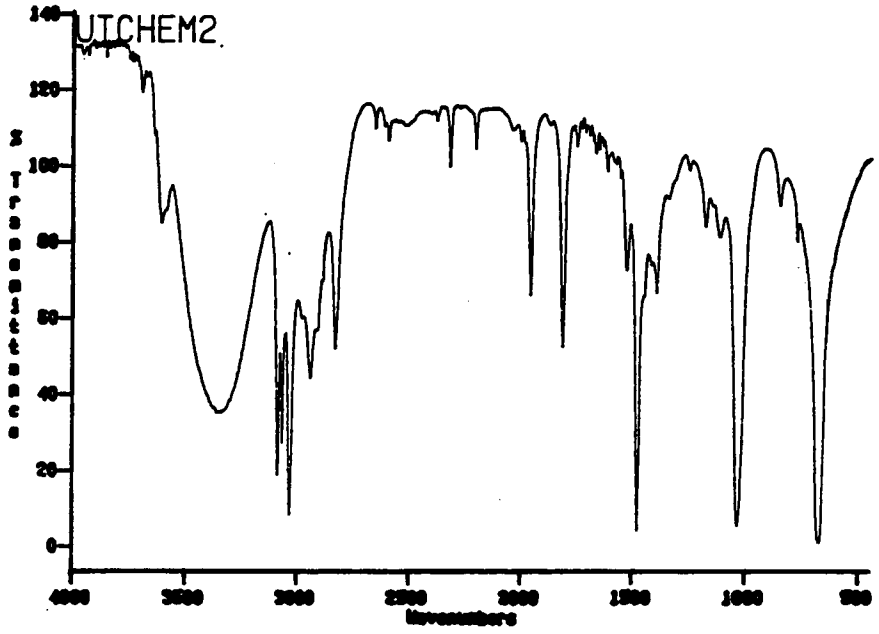


FIGURE 14. FTIR 14. Benzene-Methanol 85/15 - BM-85. The spectrum shows features of both solvents.

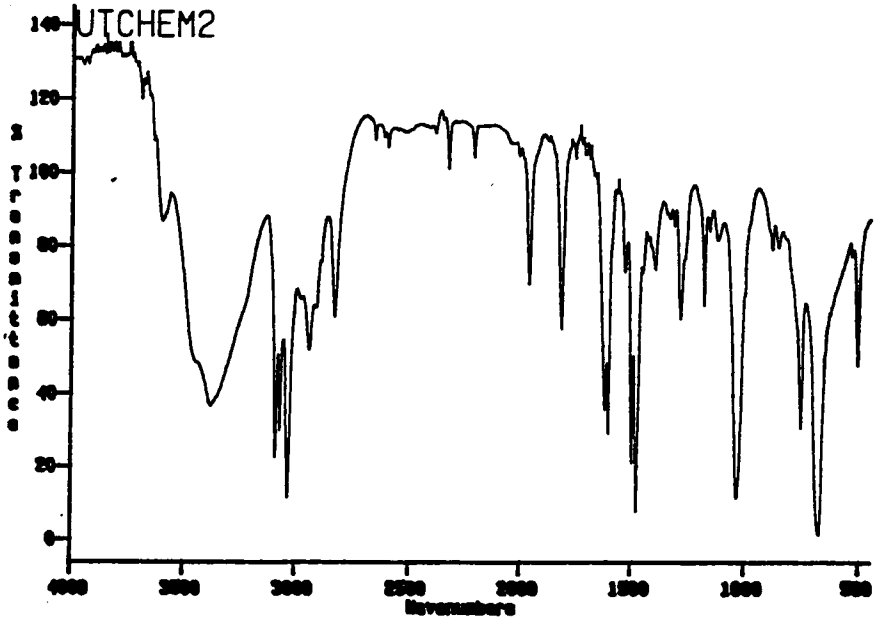


FIGURE 15. FTIR 15. 1.2N BM-85 solution of aniline. The spectrum of aniline in benzene-methanol.

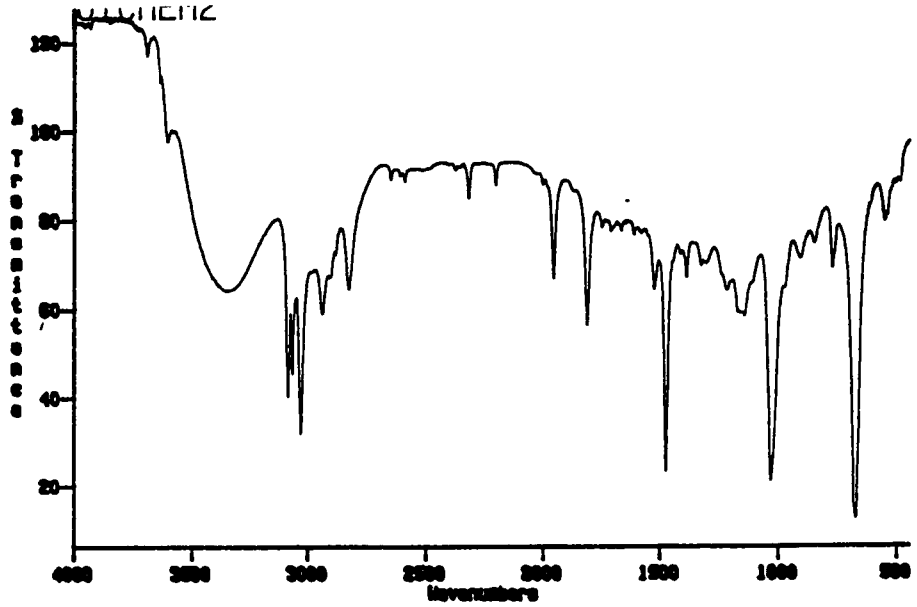


FIGURE 16. FTIR 16. 0.4N BM-85 solution of MSA.
The spectrum of methanesulfonic acid in benzene-methanol.

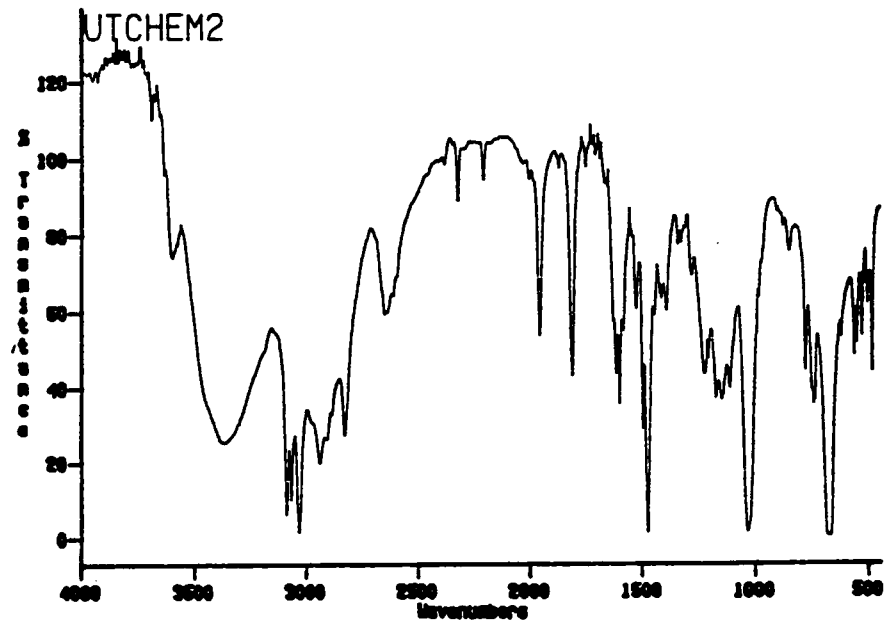


FIGURE 17. FTIR 17. BM-85 solution of aniline: MSA mix.
The mix spectrum (2 mL of 1.2N BM-85 solution of aniline and 2 mL of 0.4N BM-85 solution of MSA) in solution.

and differences in the 500-600 cm^{-1} range are observed. The subtractions were done with subtraction factors of 0.65 for aniline, 0.35 for methanesulfonic acid, and 1.0 for the mix of the two. The baseline in the subtracted spectrum determines the subtraction factor. Increasing those subtraction factors could result in the generation of inverted peaks. The subtracted spectrum for aniline is shown in Figure 18, and the aniline (pure) spectrum is shown in Figure 19. Comparing the spectra, the benzene-methanol mix proved to be the best solvent among those studied previously. Figure 20 exhibits the spectrum of the mix between methanesulfonic acid and aniline, and the same peak at about 2600 cm^{-1} appears, establishing that there is a strong interaction. Subtracted methanesulfonic acid is displayed in Figure 21, and some features of benzene such as C-H aromatic stretching (3100-3000 cm^{-1}) still arise in the spectrum.

* Choice of concentration.

The investigation for the best concentration for aniline and methanesulfonic acid was worked parallel to the search for the best ratio in the benzene-methanol mix.

The first attempt was with BM-85 as the common solvent and 0.4N solutions of aniline and methanesulfonic acid. Nine solutions (10 mL each) were prepared with different ratios (milliequivalents of aniline : milliequivalents of methanesulfonic acid):

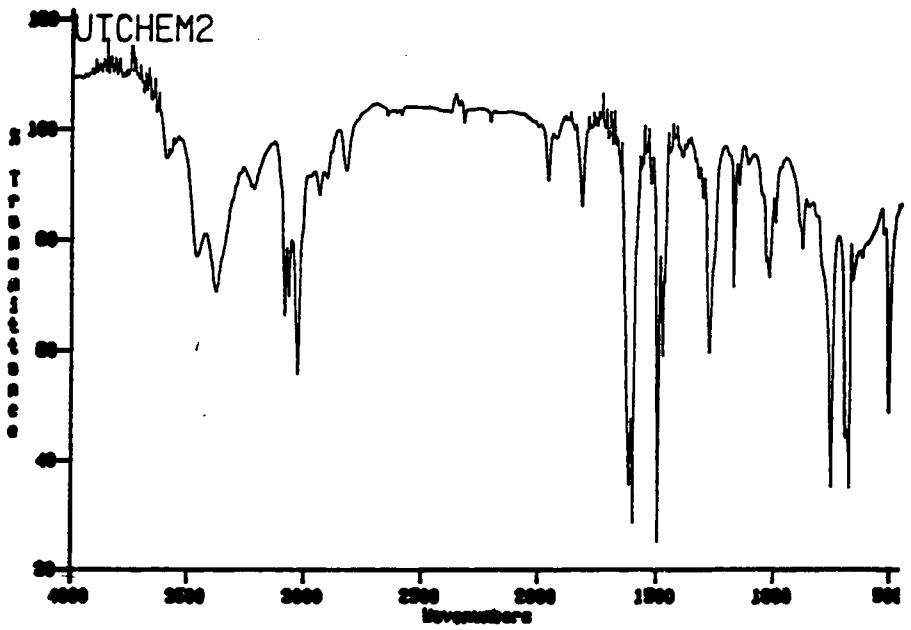


FIGURE 18. FTIR 18. Subtracted aniline (BM-85). Aniline spectrum after BM-85 subtraction from a 1.2N BM-85 solution of aniline (S.F.= 0.65).

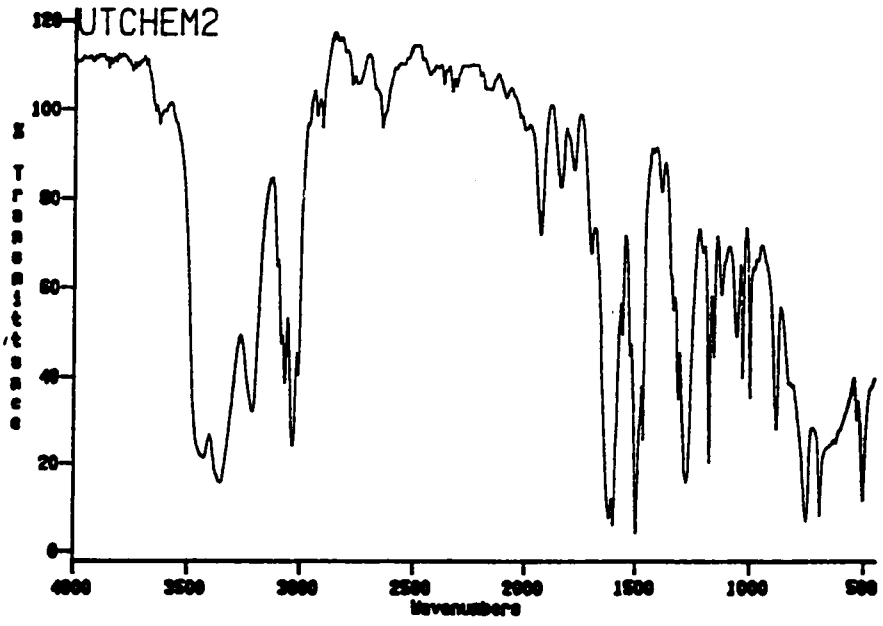


FIGURE 19. FTIR 19. Pure aniline.

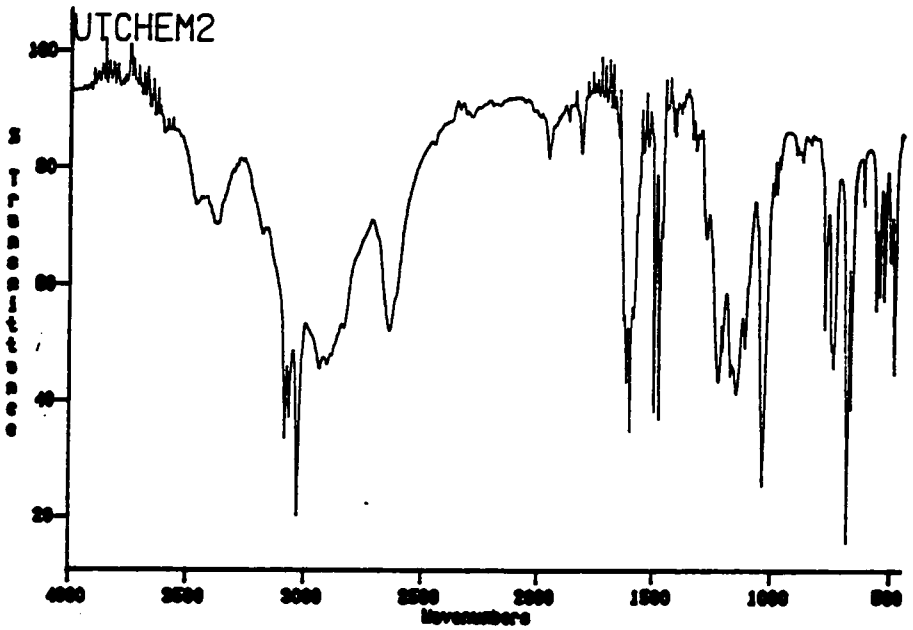


FIGURE 20. FTIR 20. Subtracted aniline: MSA mix (BM-85). The spectrum of the mix after benzene-methanol 85/15 subtraction (S.F.= 1.0).

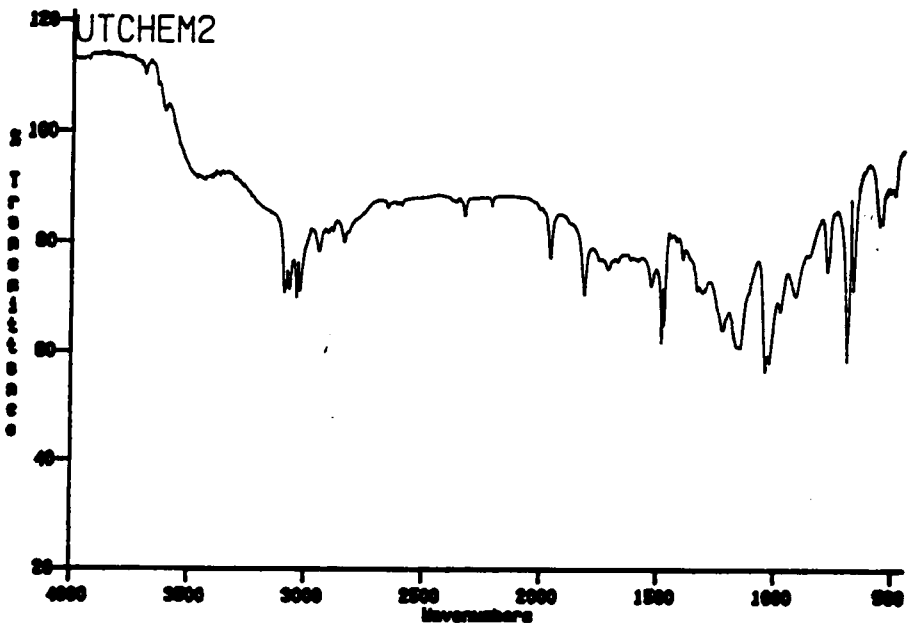


FIGURE 21. FTIR 21. Subtracted MSA (BM-85). MSA spectrum after BM-85 subtraction from a 0.4N BM-85 solution of MSA (S.F.= 0.35).

Solution	1	2	3	4	5	6	7	8	9
Ratios	1/0	5/1	2/1	1.25/1	1/1	1/1.25	1/2	1/5	0/1

From these solutions, only 1/0 (1) and 0/1 (9) remain liquid. A solid (shiny, white crystals) is formed in the other solutions. There was more precipitation in 1/1 (5), decreasing through the extremes. There is presumably a complete interaction taking place from one milliequivalent of aniline to one milliequivalent of methanesulfonic acid. To confirm the interaction, the solutions with solids were centrifuged before recording all the spectra. Figure 22 shows the 1/0 ratio (below) and the liquid portions of solutions 2 to 5. Figure 23 displays the liquid portions of solutions 5 to 8 and the 0/1 ratio (above). Those spectra are alike and have the characteristics of benzene and methanol. The subtraction (especially in 1 and 9) did not offer visible differences to compare; therefore, the concentration had to be increased. Before changing concentrations, the solid in solution 5 (1/1) was studied in nujol (mineral oil used to make a mull for IR analysis of solid compounds). The results are shown in Figure 24 (nujol spectrum), Figure 25 (mix in nujol spectrum), and Figure 26 (mix spectrum after nujol subtraction). The peak at about 2600 cm^{-1} still appears, but not clearly.

Increasing aniline concentration in BM-85 was not an

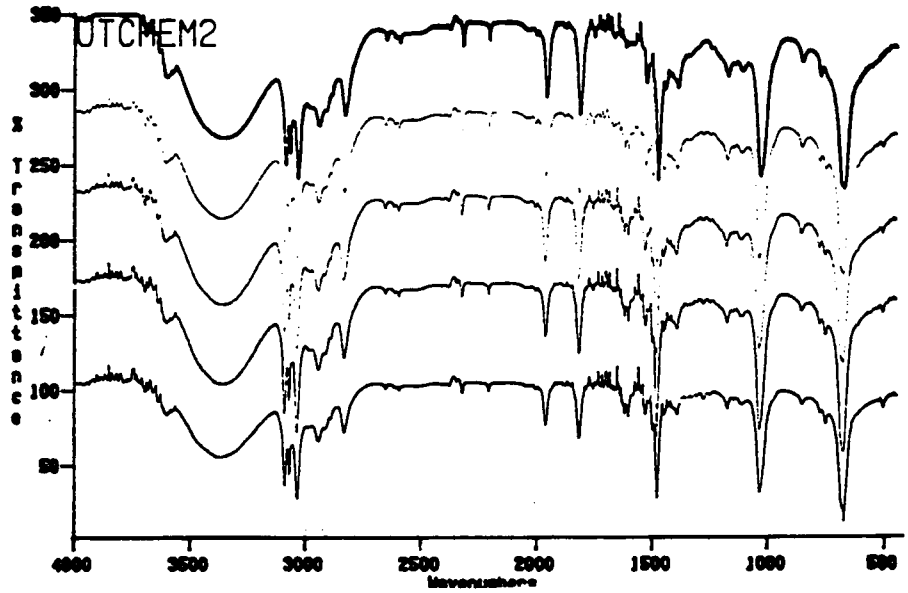


FIGURE 22. FTIR 22. Multispectral display (BM-85). The spectra of ratio 1/0 and liquid portions from 2 to 5 before solvent subtraction.

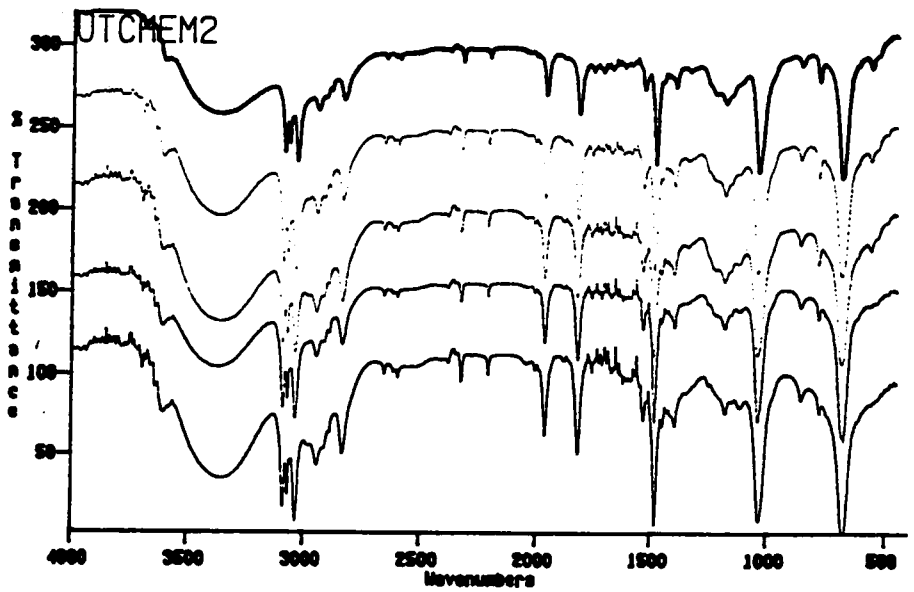


FIGURE 23. FTIR 23. Multispectral display (BM-85). The spectra of liquid portions from 5 to 8 and the ratio 0/1 before solvent subtraction.

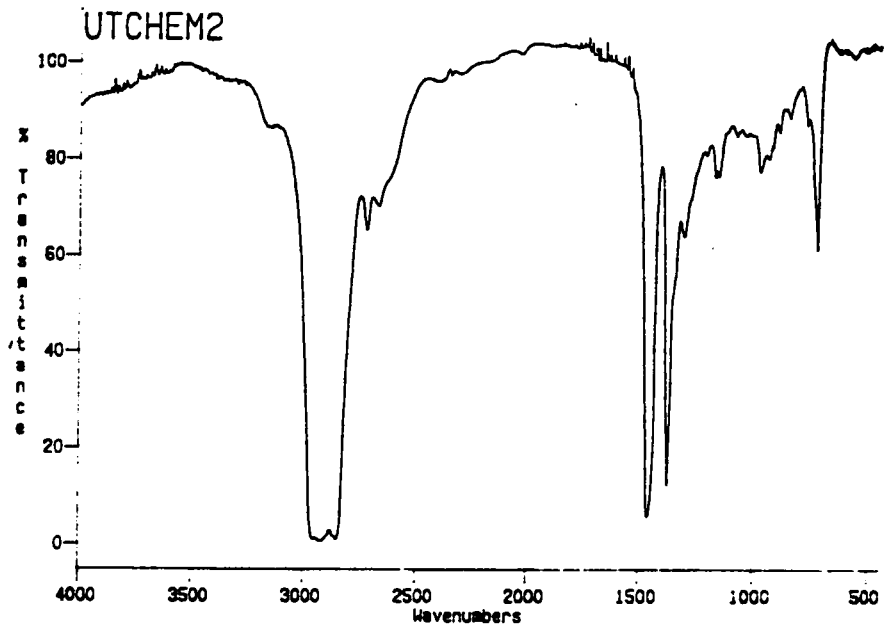


FIGURE 24. FTIR 24. Nujol spectrum.

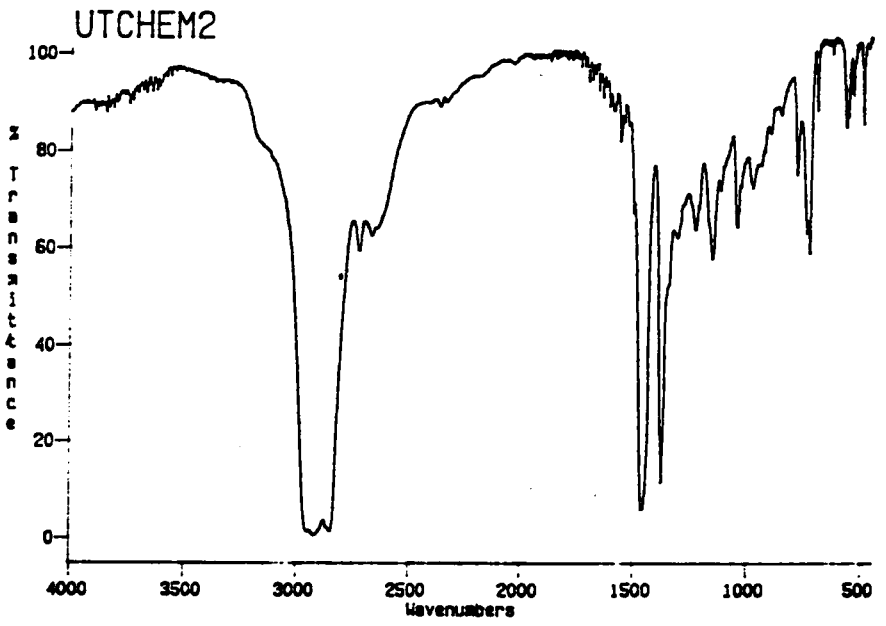


FIGURE 25. FTIR 25. Aniline: MSA mix in nujol.

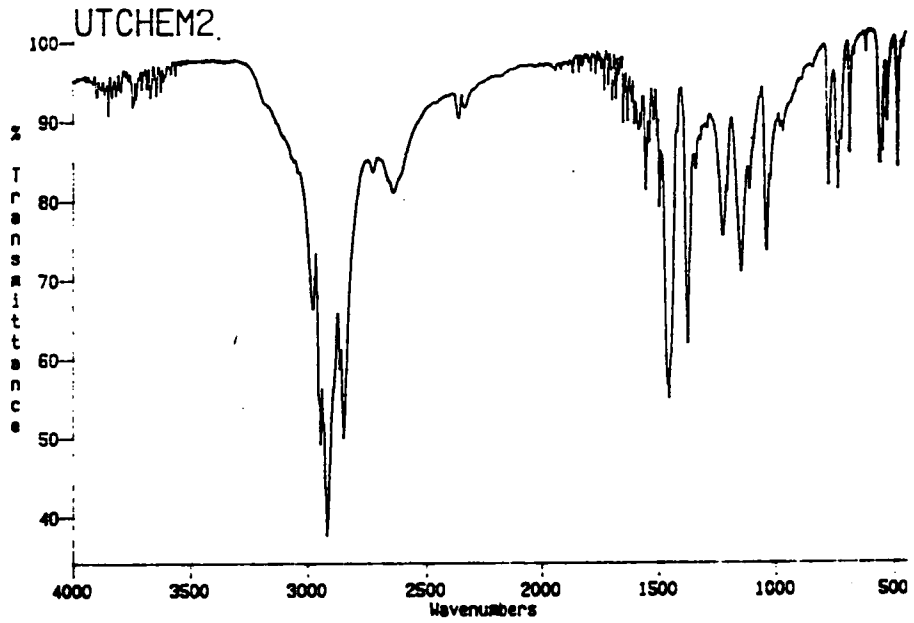


FIGURE 26. FTIR 26. Subtracted mix. The mix spectrum after nujol subtraction (S.F.= 0.8).

issue, but methanesulfonic acid cannot be dissolved unless methanol concentration is increased in the solvent mix. The study was performed with 2N BM-85 solution of aniline and 0.5N BM-85 solution of methanesulfonic acid. Aniline has a better spectrum with high concentration. Figure 27 shows the aniline spectrum after subtracting the BM-85 spectrum from the 2N BM-85 solution of aniline (the subtraction factor was 0.4). Methanesulfonic acid is seen in Figure 28, in which many of the benzene features remain after BM-85 is subtracted.

As a consequence, some of the alternatives are higher aniline concentration, or lower benzene percentage in the solvent (higher methanol percentage in the mix) in order to increase the methanesulfonic acid concentration.

The next study in the search for concentrations was done with aniline 4N and methanesulfonic acid 0.5N in benzene-methanol mix with ratio 80/20 named BM-80. After subtraction for aniline (S.F.= 0.6), an acceptable spectrum is obtained, as shown in Figure 29. It is a satisfactory subtraction and the spectrum is similar to the standard. Regarding methanesulfonic acid, its spectrum is displayed in Figure 30 and benzene traces are observed. When the concentration of methanesulfonic acid was incremented to 1N, the solution became opaque; therefore, the answer to get a satisfactory methanesulfonic acid spectrum is either to lower the acid concentration or to increase the

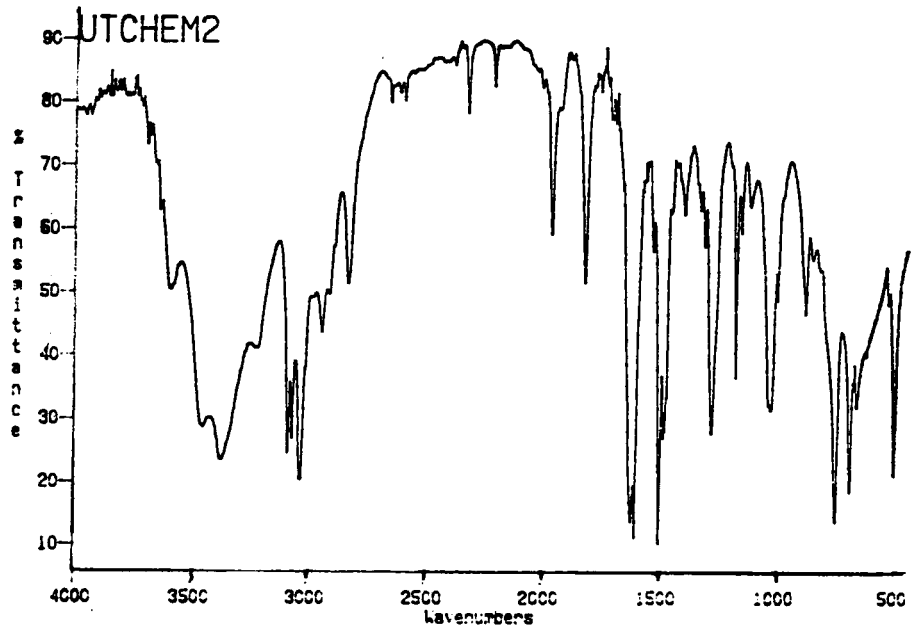


FIGURE 27. FTIR 27. Subtracted aniline (BM-85). Aniline spectrum after BM-85 subtraction from a 2N BM-85 solution of aniline (S.F.= 0.4).

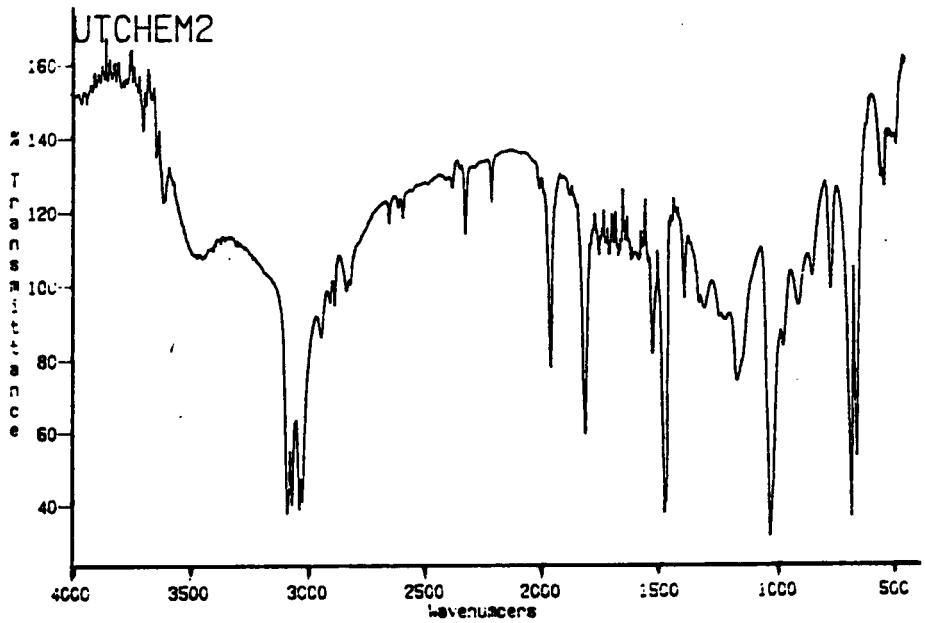


FIGURE 28. FTIR 28. Subtracted MSA (BM-85). MSA spectrum after BM-85 subtraction from a 0.5N BM-85 solution of MSA (S.F.= 0.5).

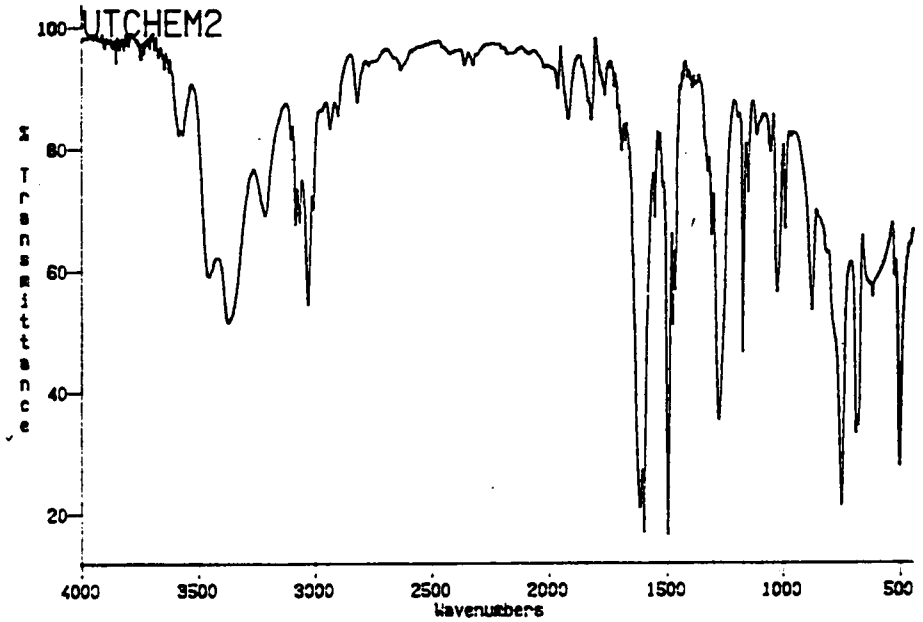


FIGURE 29. FTIR 29. Subtracted aniline (BM-80). Aniline spectrum after BM-80 subtraction from a 4N BM-80 solution of aniline (S.F.= 0.6).

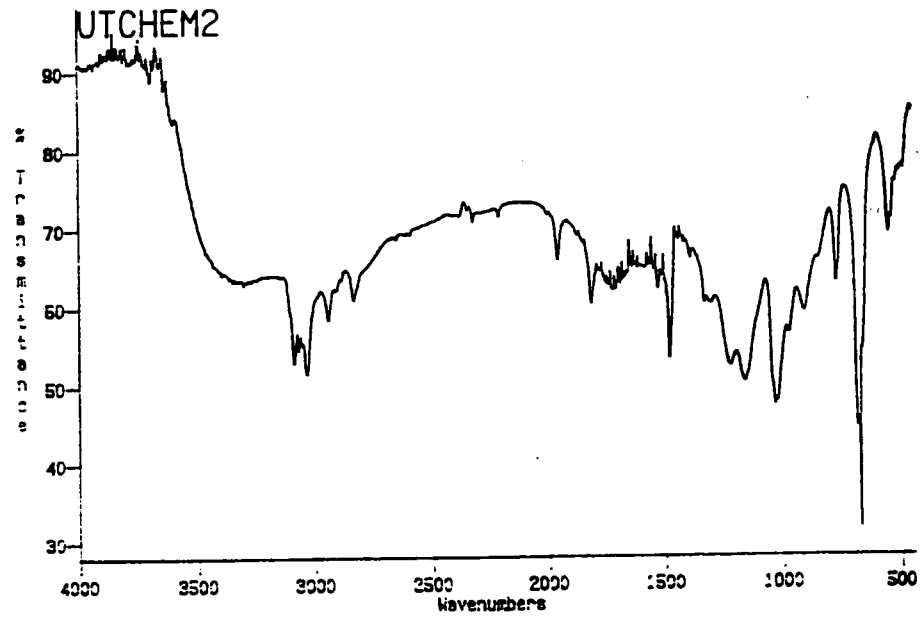


FIGURE 30. FTIR 30. Subtracted MSA (BM-80). MSA spectrum after BM-80 subtraction from a 0.5N BM-80 solution of MSA (S.F.= 0.4).

methanol percentage in the solvent. This was considered a better option.

The final study was completed working with BM-75 as the solvent, 4N BM-75 solution of aniline, and 0.8N BM-75 solution of methanesulfonic acid. The increase of methanol percentage in the solvent mix permits the increase of methanesulfonic acid concentration.

From the original BM-75 solutions of aniline and methanesulfonic acid, three solutions were prepared with the following ratios:

Sol 1S: aniline (1 meq.) : methanesulfonic acid (0 meq.)
Sol 2S: aniline (1 meq.) : methanesulfonic acid (1 meq.)
Sol 3S: aniline (0 meq.) : methanesulfonic acid (1 meq.)

Figure 31 exhibits a multispectral display of the solvent BM-75 (above), the 4N BM-75 solution of aniline (middle), and the 0.8N BM-75 solution of methanesulfonic acid (below). It is possible to observe differences among the spectra. The three dilutions (1S, 2S, 3S) were recorded in Figure 32. Notice that the mix (1 meq. each) displays a strong peak at about 2600 cm^{-1}, even prior to the BM-75 subtraction. The subtracted spectra are shown in Figure 33, where the three compounds have completely different characteristics.

Every dilution was plotted with its respective subtraction. Figure 34 corresponds to BM-75 solution of ani-

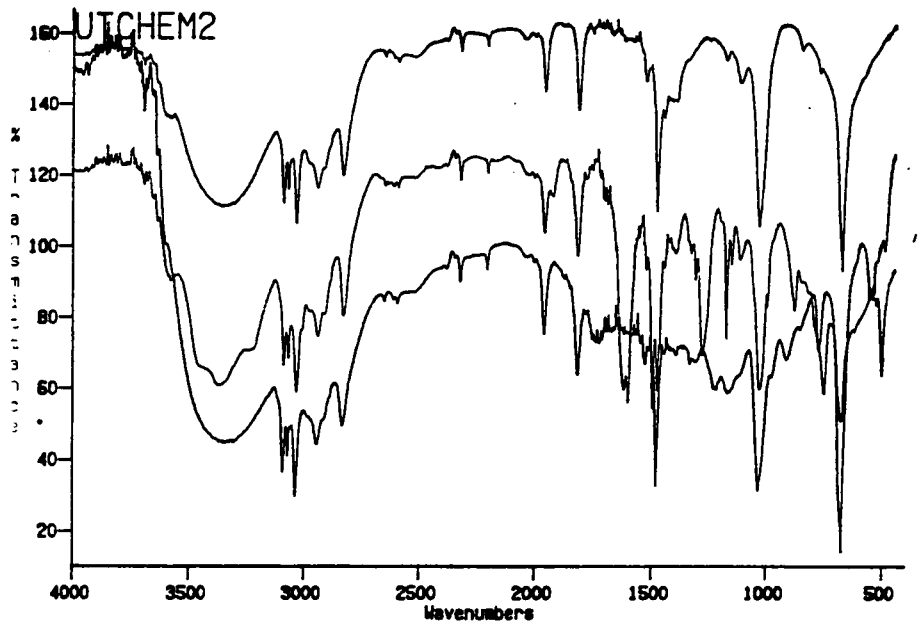


FIGURE 31. FTIR 31. Multispectral display. BM-75 (above). 4N BM-75 solution of aniline (middle). 0.8N BM-75 solution of MSA (below).

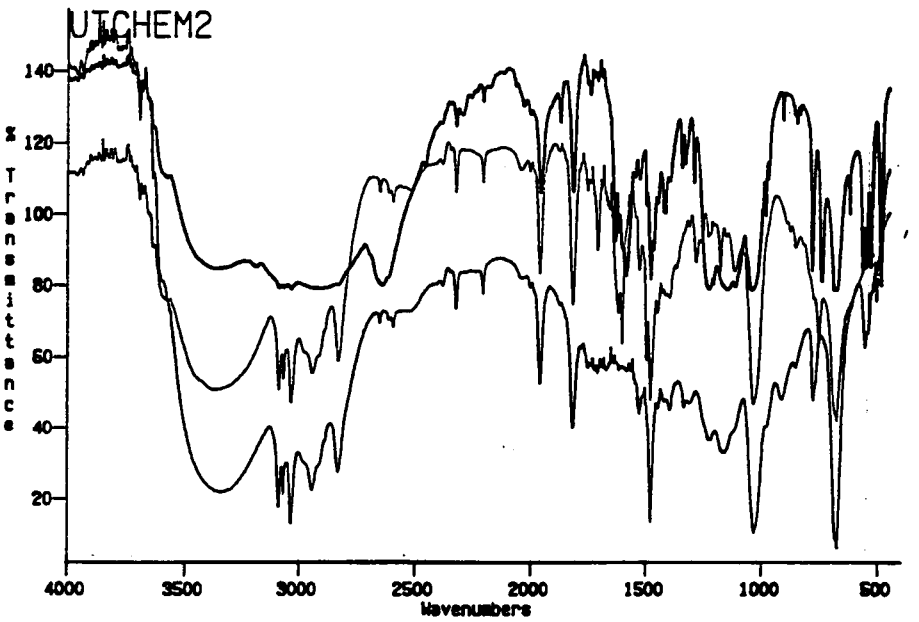


FIGURE 32. FTIR 32. Multispectral display: 1S, 2S, 3S. BM-75 solutions of aniline, MSA, and mix (1 meq. of aniline and 1 meq. of MSA).

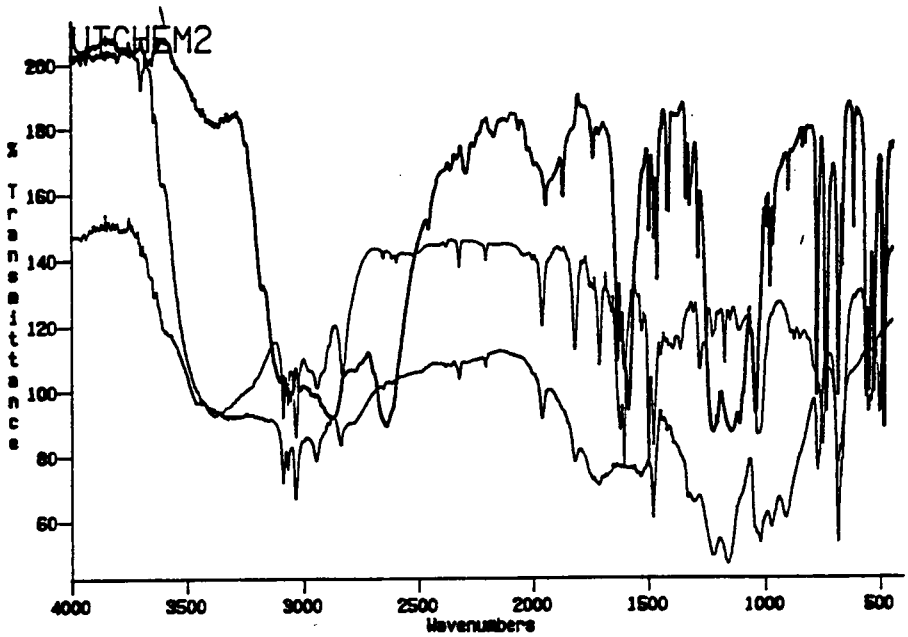


FIGURE 33. FTIR 33. Subtracted 1S, 2S, 3S. The spectra after BM-75 subtraction. The mix forms a new peak at about 2600 cm^{-1}.

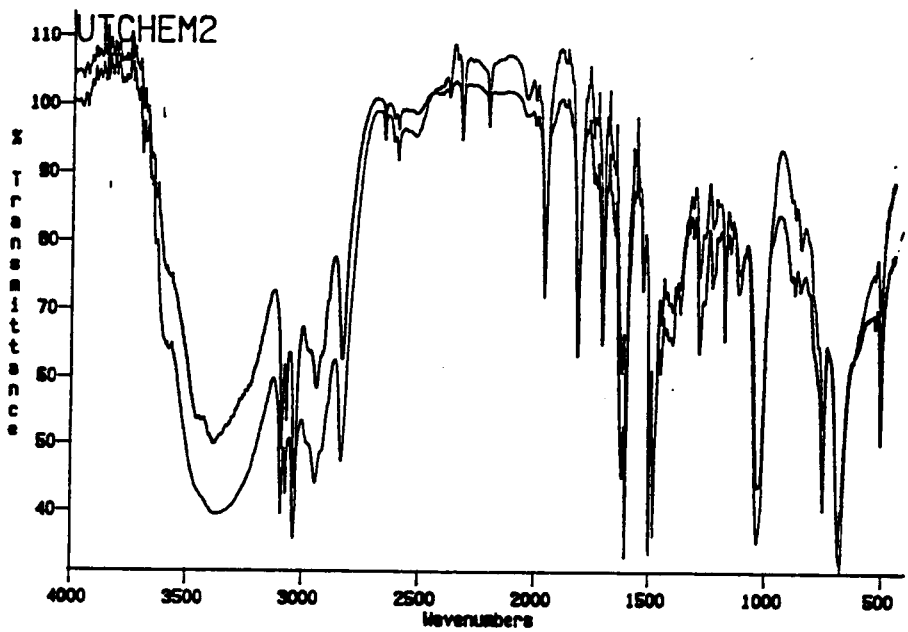


FIGURE 34. FTIR 34. Aniline in BM-75 / Subtracted aniline (S.F.= 1.3).

line and the subtracted spectrum above. Figure 35 displays the BM-75 solution of the two compounds and the mix spectrum, which does not show the O-H band at about 3300 cm^{-1} but a very strong peak at about 2600 cm^{-1}. Figure 36 reveals the BM-75 solution of methanesulfonic acid and the subtracted spectrum. It was difficult to obtain an acceptable spectrum for this compound. A comparison is shown in Figure 37 in which the lower spectrum corresponds to pure methanesulfonic acid (a tiny drop) and the upper spectrum corresponds to subtracted methanesulfonic acid from the BM-75 solution. The latter shows some traces of benzene-methanol.

After the selection of aniline concentration (4N), methanesulfonic acid concentration (0.8N), and solvent mix ratio (BM-75), nine dilutions were prepared with different ratios (milliequivalents of aniline : milliequivalents of methanesulfonic acid) as in an earlier attempt:

Solutions	1	2	3	4	5	6	7	8	9
Ratios	1/0	5/1	2/1	1.25/1	1/1	1/1.25	1/2	1/5	0/1

Solutions 1 and 9 remain liquid. Solutions 2 to 8 produce very shiny, white crystals. Solution 5 has more precipitation than the other solutions. The best way to discover whether or not the interaction is complete with

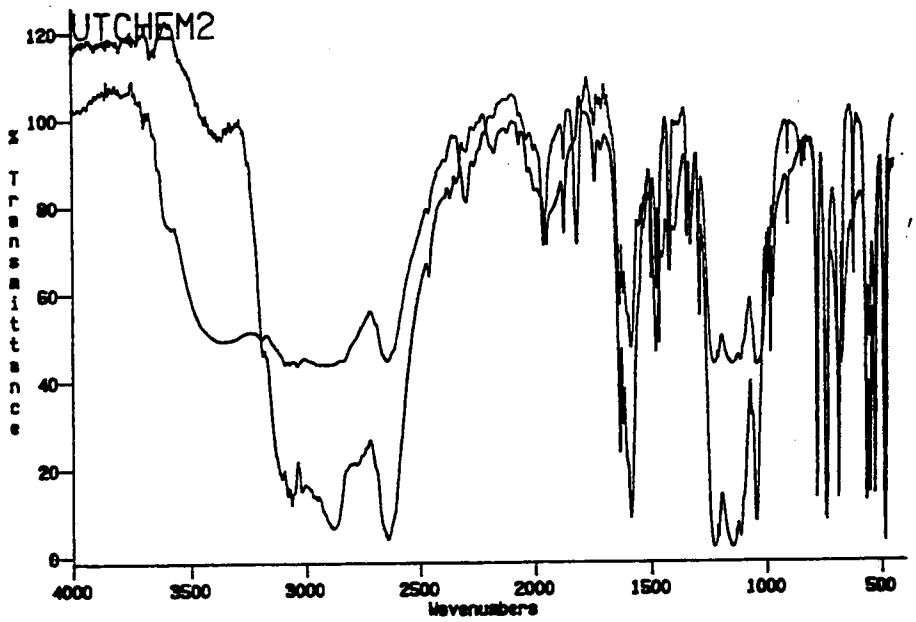


FIGURE 35. FTIR 35. Mix in BM-75 / Subtracted mix. The subtraction factor is determined from the display field (S.F.= 2.4).

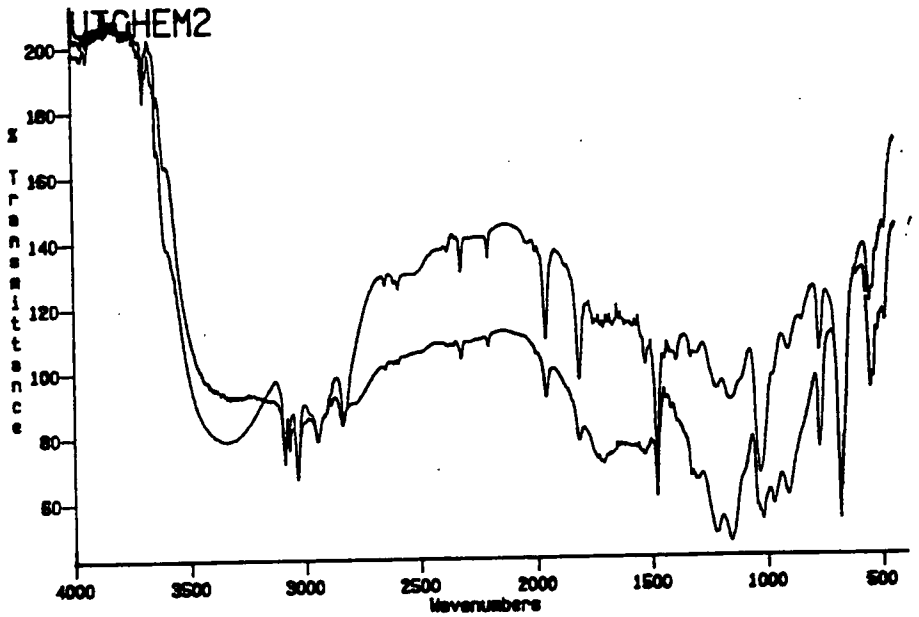


FIGURE 36. FTIR 36. MSA in BM-75 / Subtracted MSA. (S.F.= 1.3.)

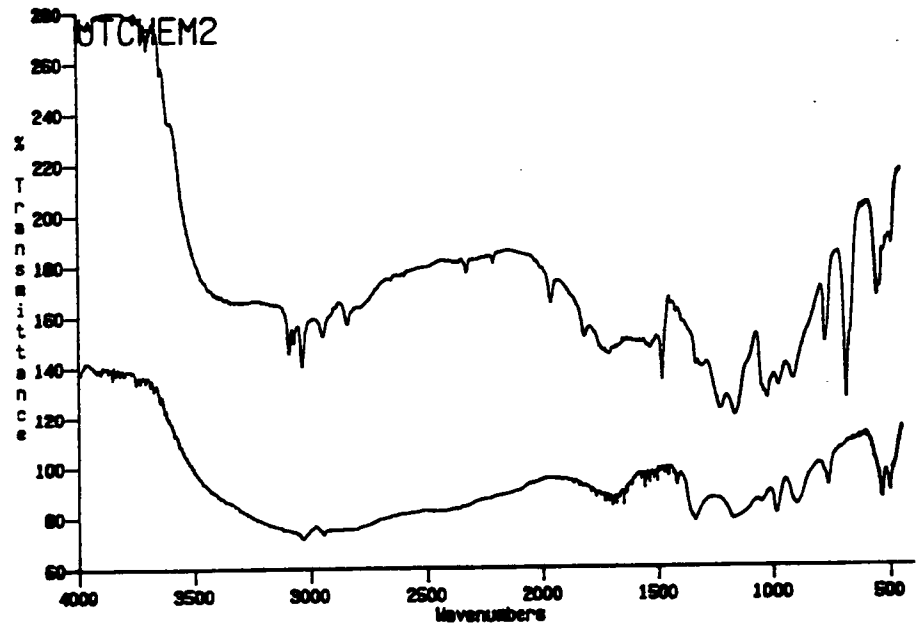


FIGURE 37. FTIR 37. Subtracted MSA / Pure MSA. The subtracted spectrum from figure 36 is shown above. The pure compound.(a tiny drop) spectrum is shown below.

one milliequivalent each is by centrifugation of the solutions with some solid, and by analyzing each phase: liquid (named TOP or T) and solid (named BOTTOM or B). The extremes were called 1TB and 9TB.

Figure 38 exhibits a multispectral display with nine spectra: 1TB (aniline in BM-75) is the lower spectrum. 9TB (methanesulfonic acid in BM-75) is the upper spectrum. Between those two spectra, 2T to 8T (liquid portions of solutions) are shown. All look alike. They are similar to BM-75 spectrum displayed in Figure 39.

Benzene was used to smear the solid portion of each mix because methanol subtraction is more difficult. The bottom portions (in benzene) are displayed in Figure 40. After BM-75 subtraction in 1TB, 2T through 8T and 9TB, it becomes feasible to understand the interaction between aniline and methanesulfonic acid:

*Figure 41. An important feature to follow is a peak at about 1600 cm^{-1} corresponding to N-H bending from aniline.

*Figure 42. The N-H bending has a strong signal (proportional to concentration).

*Figure 43. It shows a less strong band at about 1600 cm^{-1}.

*Figure 44. The aniline traces have almost disappeared.

*Figure 45. 5T-BM. The peak disappeared. Therefore, the interaction is complete at this ratio and the liquid portion is all BM-75.

Compare with BM-75 spectrum in Figure 39.

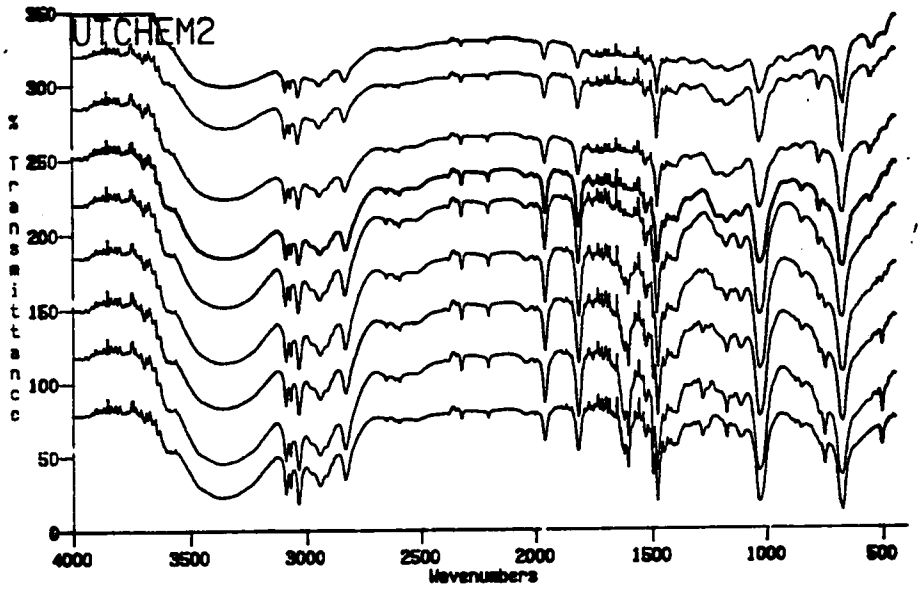


FIGURE 38. FTIR 38. Multispectral display. There is a small difference at about 2600 cm^{-1}, but they look alike. The solvent is BM-75.

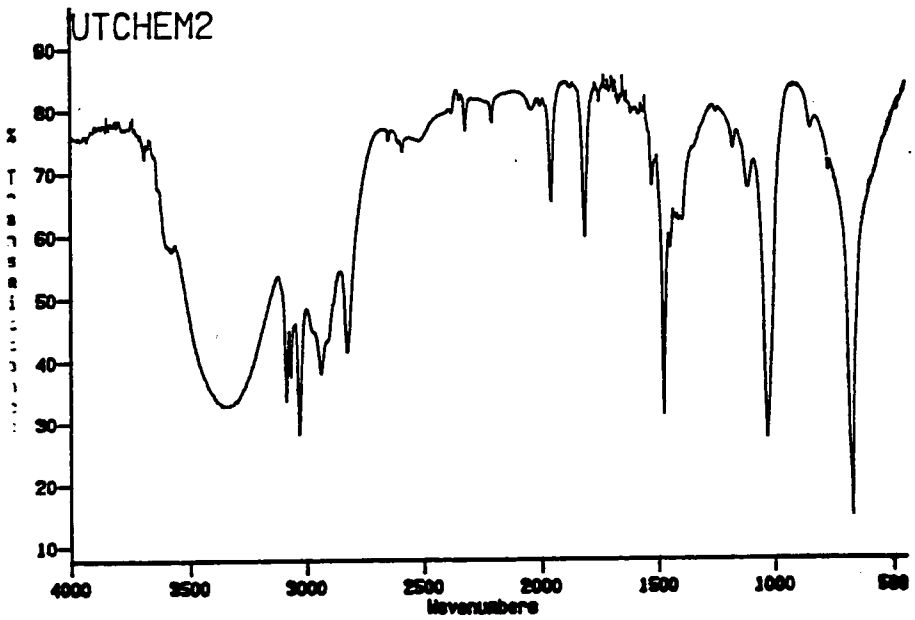


FIGURE 39. FTIR 39. Benzene-Methanol 75/25 spectrum. This is the BM-75 spectrum selected to study the interactions in this research.

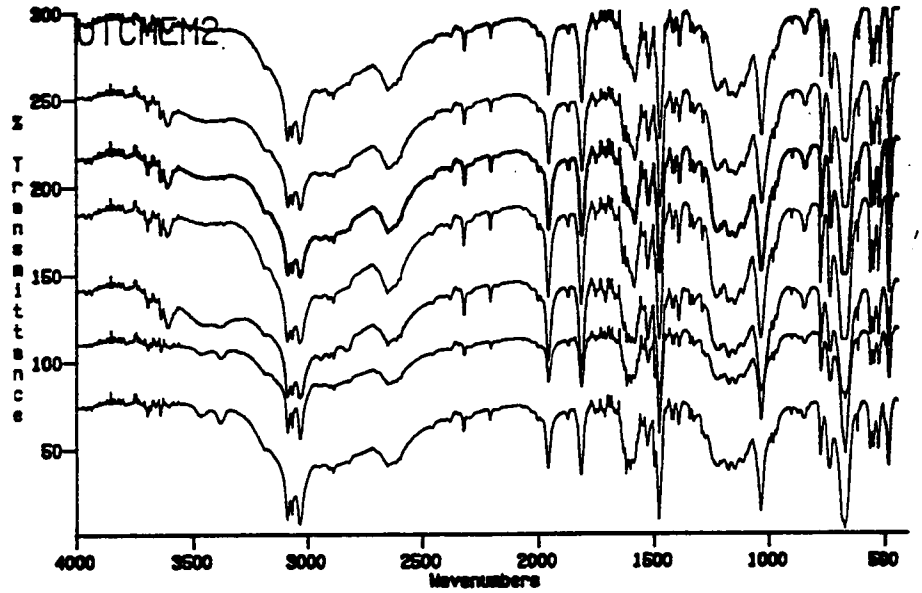


FIGURE 40. FTIR 40. Multispectral display. The spectra of the seven dispersions (solid portions in benzene) show the new peak at about 2600 cm^{-1}.

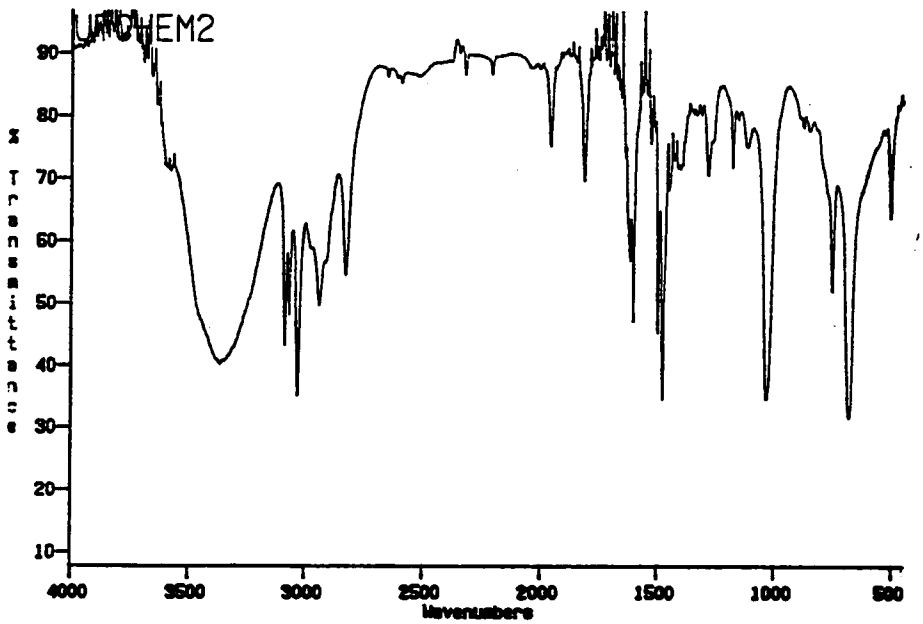


FIGURE 41. FTIR 41. 1TB-BM. Subtracted ratio 1/0. This is aniline spectrum with BM-75 traces.

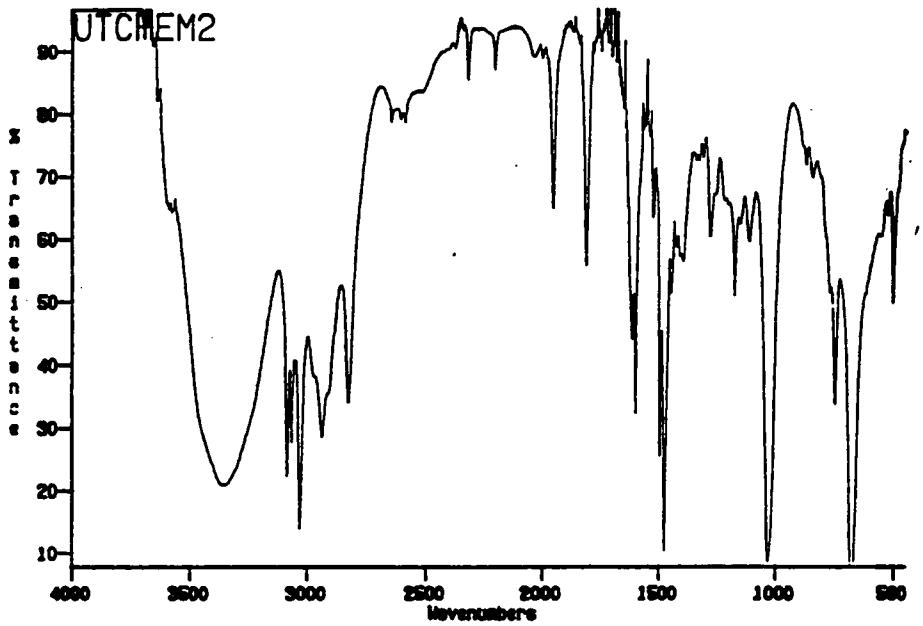


FIGURE 42. FTIR 42. 2T-BM. Liquid portion of ratio 5/1. BM-75 (plus unreacted aniline because of its excess) spectrum after subtraction.

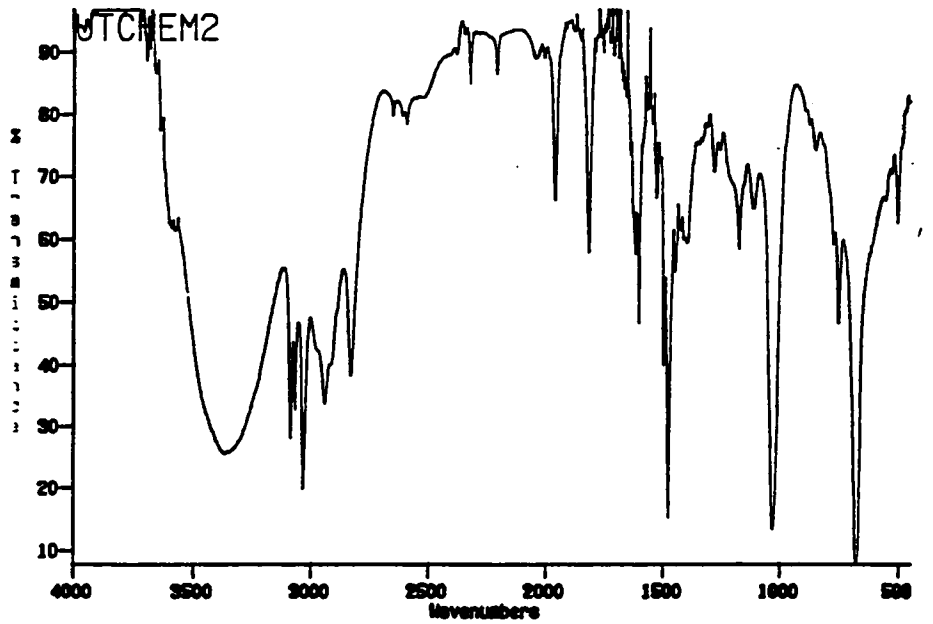


FIGURE 43. FTIR 43. 3T-BM. Liquid portion of ratio 2/1. BM-75 (plus unreacted aniline) spectrum after subtraction.

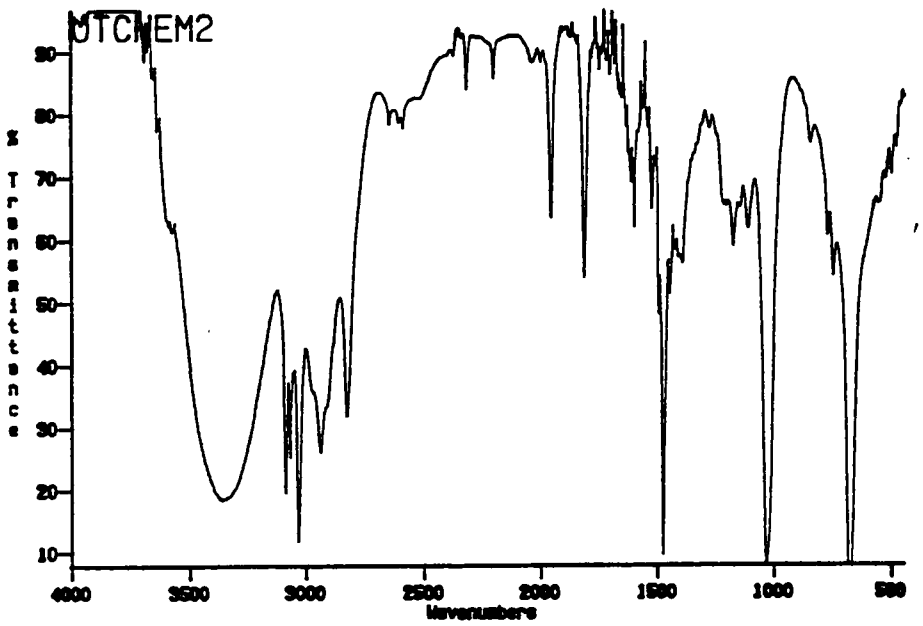


FIGURE 44. FTIR 44. 4T-BM. Liquid portion of ratio 1.25/1. (After solvent subtraction.)

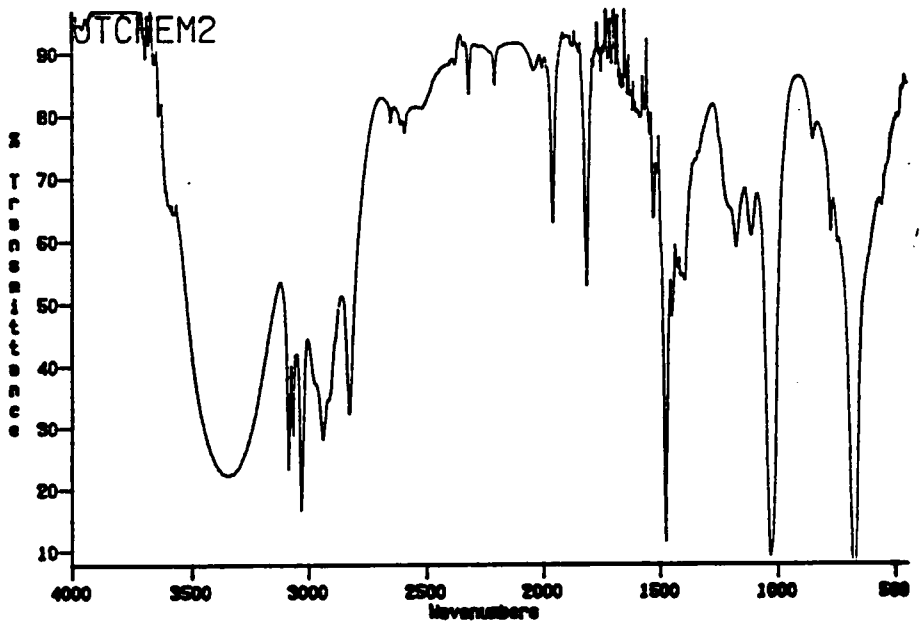


FIGURE 45. FTIR 45. 5T-BM. Liquid portion of ratio 1/1. This spectrum (after solvent subtraction) and BM-75 spectrum (figure 39) look alike.

*Figure 46. This spectrum exhibits a baseline fall. There are some methanesulfonic acid traces combined with BM-75.

*Figure 47. As the methanesulfonic acid proportion increases in the mix, there is more unreacted compound that is proved by the baseline fall.

*Figure 48. The spectrum displays BM-75 and methanesulfonic acid traces.

*Figure 49. This is mostly methanesulfonic acid with BM-75 traces.

Regarding the solid portion, seven spectra were recorded called #B-BENZ. Figures 50 - 56 display the mix spectrum at seven different ratios: 5/1 (Figure 50), 2/1 (Figure 51), 1.25/1 (Figure 52), 1/1 (Figure 53), 1/1.25 (Figure 54), 1 /2 (Figure 55), 1/5 (Figure 56). It seems that the strongest peak at about 2600 cm^{-1} occurs in 5B-BENZ (Figure 53). Consequently, the interaction between aniline and methanesulfonic acid is complete at a ratio of a milliequivalent of aniline to a milliequivalent of methanesulfonic acid.

* Model Compound Studies.

Aniline : Methanesulfonic acid. The interaction within these compounds was studied earlier.

Aniline. (See Figure 57.) Aniline is a highly toxic, aromatic compound, cancer suspect agent, with molecular for-

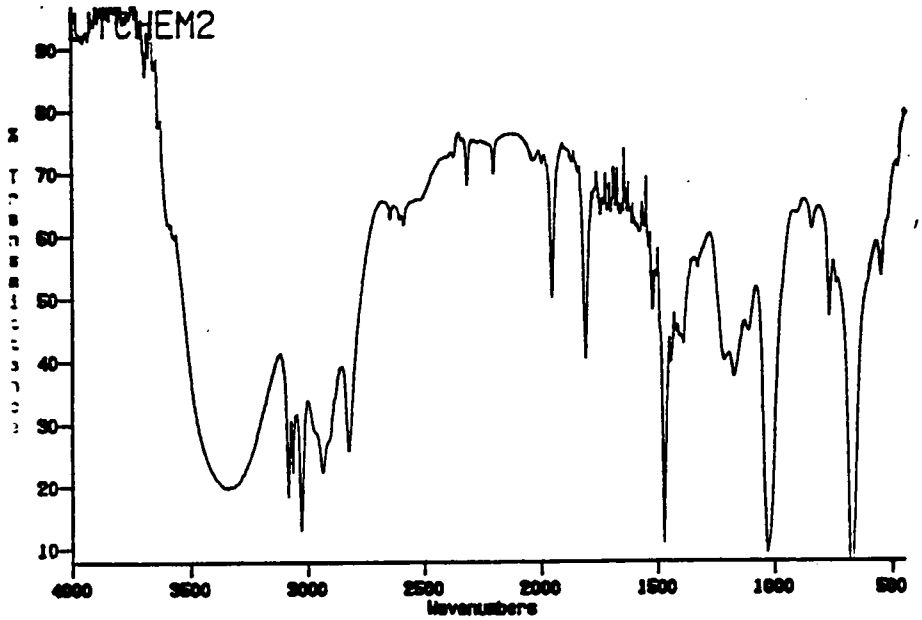


FIGURE 46. FTIR 46. 6T-BM. Liquid portion of ratio 1/1.25. BM-75 with MSA traces (after solvent subtraction).

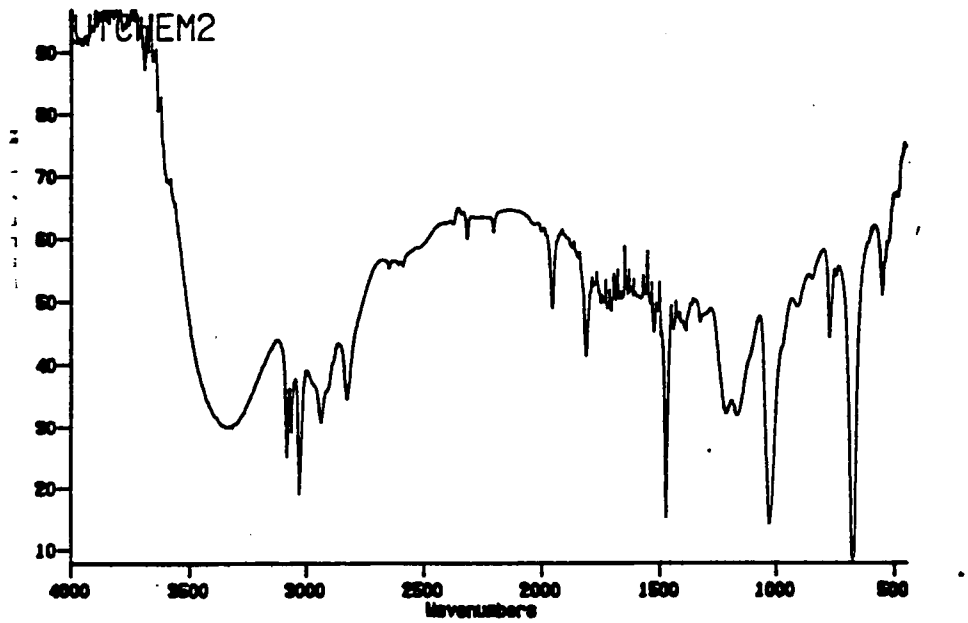


FIGURE 47. FTIR 47. 7T-BM. Liquid portion of ratio 1/2. The baseline fall proves the MSA excess (after solvent subtraction).

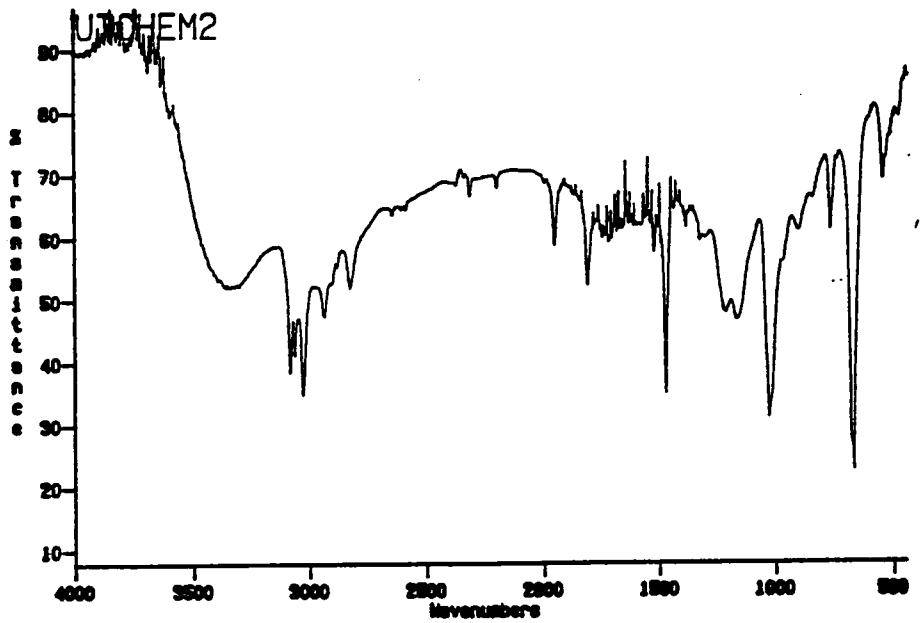


FIGURE 48. FTIR 48. 8T-BM. Liquid portion of ratio 1/5. After BM-75 subtraction, MSA excess is shown in the figure.

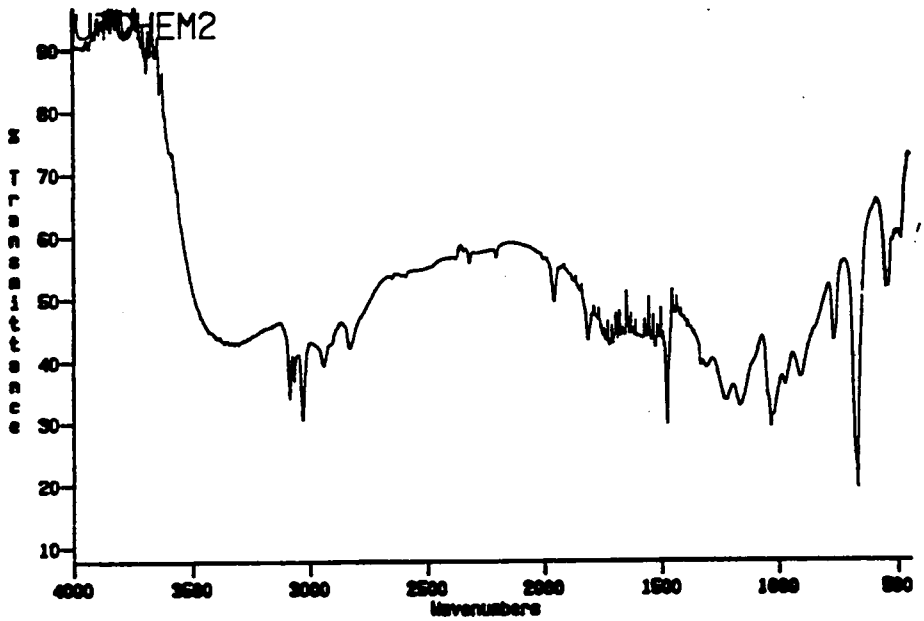


FIGURE 49. FTIR 49. 9T-BM. Subtracted ratio 0/1. MSA spectrum (with BM-75 traces).

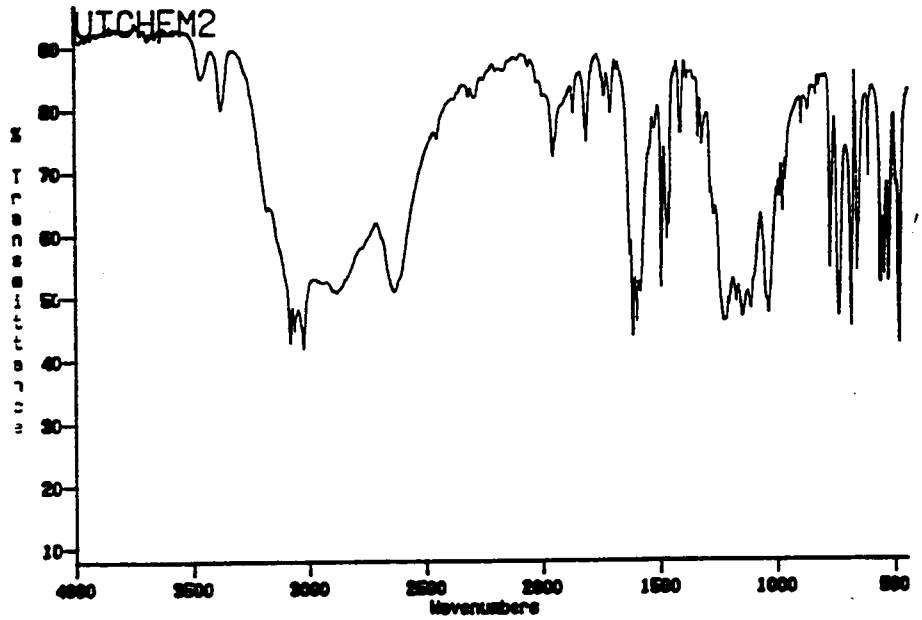


FIGURE 50. FTIR 50. Subtracted solid portion of 5/1. Aniline : MSA mix.

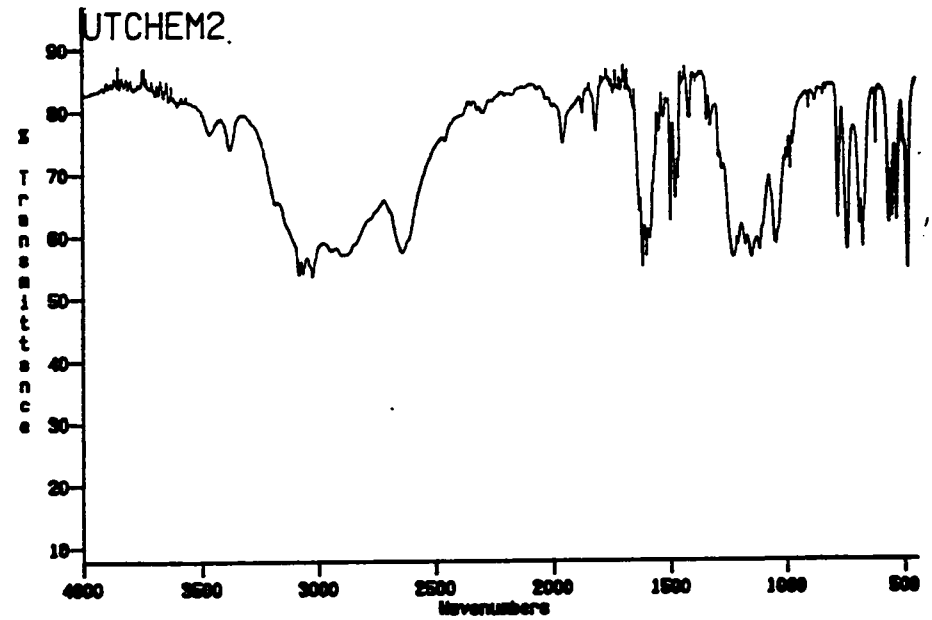


FIGURE 51. FTIR 51. Subtracted solid portion of 2/1. Aniline : MSA mix.

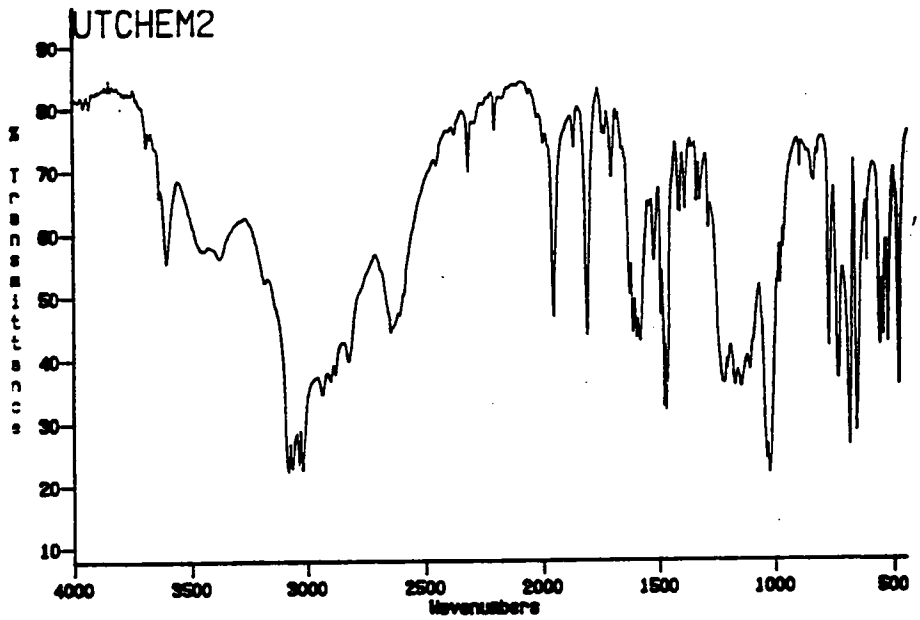


FIGURE 52. FTIR 52. Subtracted solid portion of 1.25/1. Aniline : MSA mix.

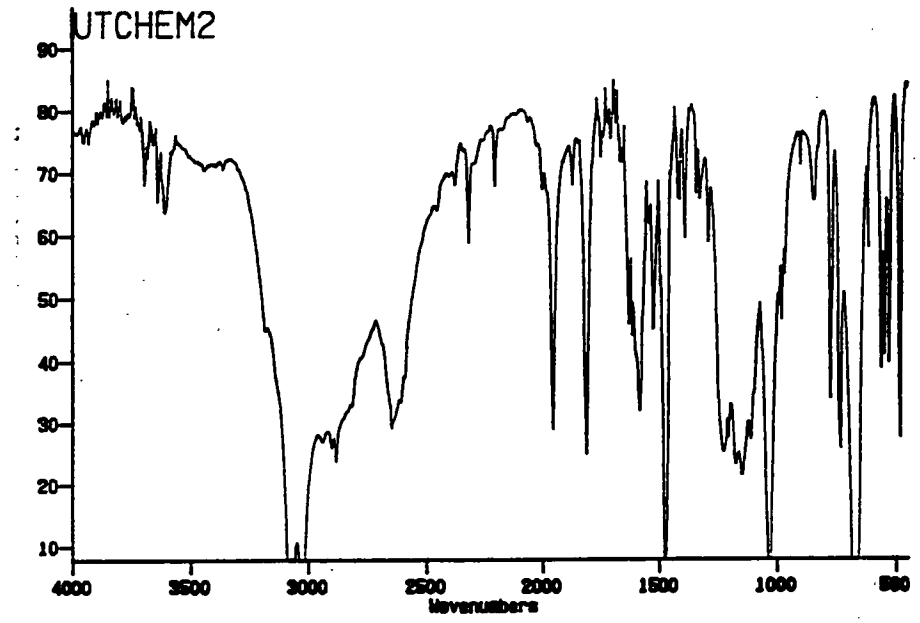


FIGURE 53. FTIR 53. Subtracted solid portion of 1/1. Aniline : MSA mix (complete reaction).

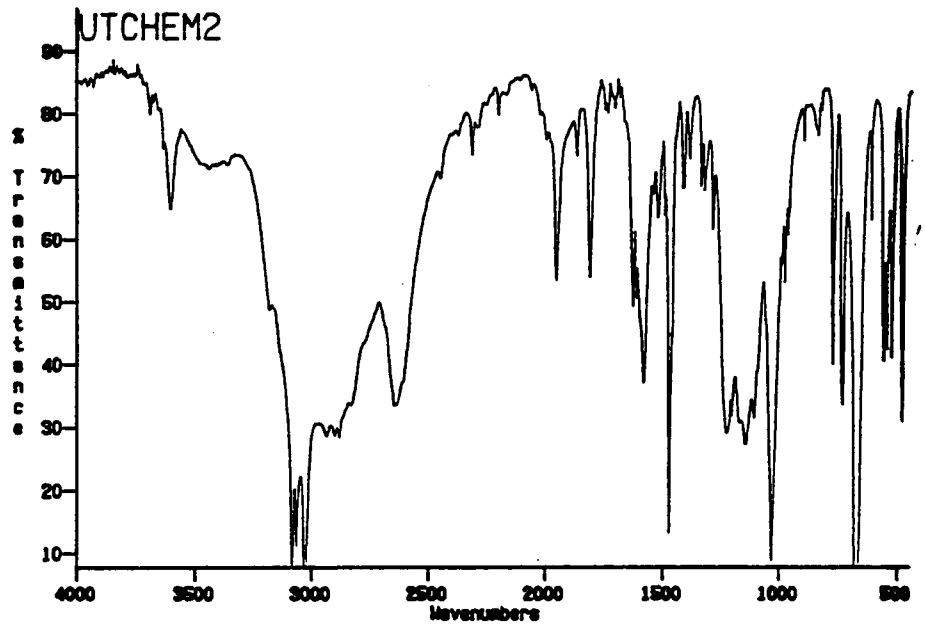


FIGURE 54. FTIR 54. Subtracted solid portion of 1/1.25. Aniline : MSA mix.

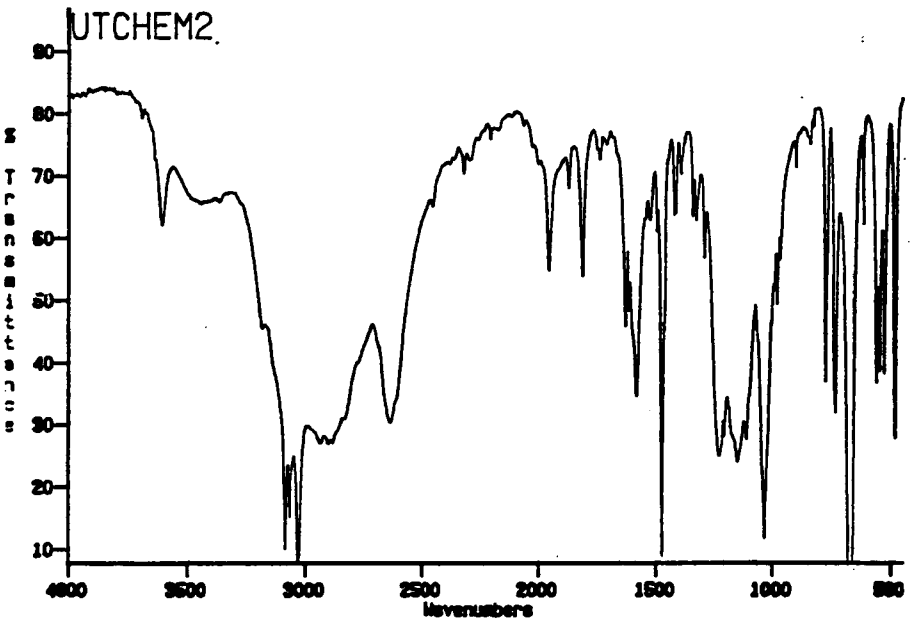


FIGURE 55. FTIR 55. Subtracted solid portion of 1/2. Aniline : MSA mix.

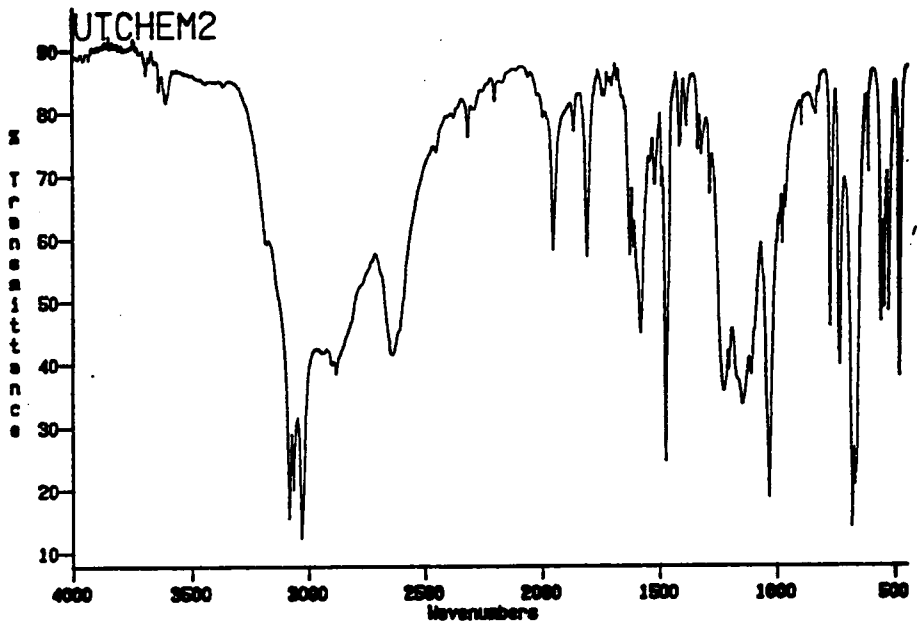


FIGURE 56. FTIR 56. Subtracted solid portion of 1/5. Aniline : MSA mix.

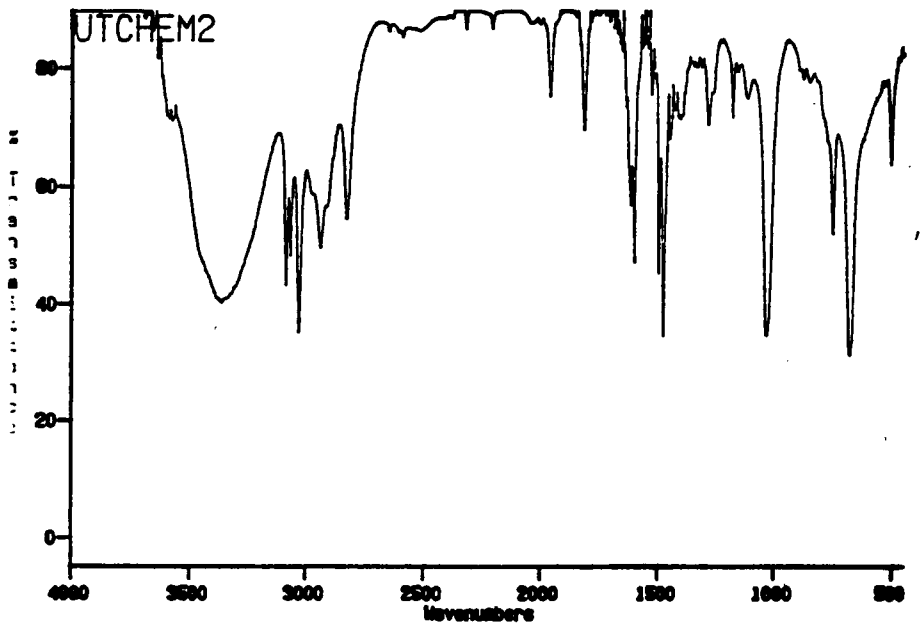


FIGURE 57. FTIR 57. Subtracted aniline. 1TB-BM (figure 41) with a different transmittance scale.

mula $C_6H_5NH_2$. Aniline spectrum shows the following bands and peaks:

-The N-H asymmetric and symmetric stretching frequencies occur at 3520 and 3400 cm^{-1}. Experimentally, there is a band with center at 3361 cm^{-1} (no resolution because of solvent subtraction) that involves the two N-H stretching frequencies.

-The C-H aromatic stretching occurs at 3100-3000 cm^{-1}. Peaks at 3093, 3070, and 3035 were obtained. The peaks at 2937 and 2826 cm^{-1} correspond to C-H stretching from methylene and methyl groups (probably from methanol).

-The N-H bending is observed about 1650-1580 cm^{-1}. There is a peak at 1618 cm^{-1} in the spectrum.[26,29]

-The C-C stretching in the ring frequency shows three peaks at 1610, 1497, and 1453 cm^{-1}. Three peaks were obtained experimentally: one peak at 1610 cm^{-1}; the other two at about 1481 cm^{-1}.

-The C-N stretch and the N-H bending are weak at 1250 cm^{-1}. A small peak at 1279 cm^{-1} is obtained.

-The C-H in plane ring bending is about 1208 cm^{-1}. The peak in the spectrum is at 1172 cm^{-1}.

-The C-N stretch appears at 1063 cm^{-1}. In this spectrum, it is displayed at 1030 cm^{-1}.

-The C-H aromatic out of plane ring bending that is usually at 735 cm^{-1} appears at 750 cm^{-1}.

-There is a broad band between 800-666 cm^{-1} which corre-

sponds to the N-H wagging.

-The C-C bend ring frequency is commonly at 697 cm^{-1}. It is shown at 680 cm^{-1} in the spectrum.

-In plane and out of plane ring deformation for benzene derivatives show two bands between 580 and 420 cm^{-1}. A peak at 505 cm^{-1} is experimentally obtained.[26]

-Peaks at 1958 and 1814 cm^{-1} are overtone bands displayed by aromatic compounds.

Methanesulfonic Acid. (See Figure 58.) It is a very strong acid and its spectrum is not known. This spectrum is not acceptable but it was the best spectrum obtained by subtraction. Methanesulfonic acid is a very corrosive compound with molecular formula CH_3SO_3H.

The following bands and peaks were obtained in the subtracted spectrum:

-A broad band with center at 3354 cm^{-1} is due to the O-H stretching (intermolecular hydrogen bonded).

-Peaks at about 3100-3000 cm^{-1} remain from solvent (C-H aromatic stretching from benzene).

-Peaks at 2945 and 2833 cm^{-1} are due to the C-H stretching of methyl group in the compound (and also remaining from methanol in the solvent).

-Two peaks are observed at about 1322 cm^{-1}. S=O stretching occurs at 1350-1342 cm^{-1}. O-H in plane bending is also at that range.[29]

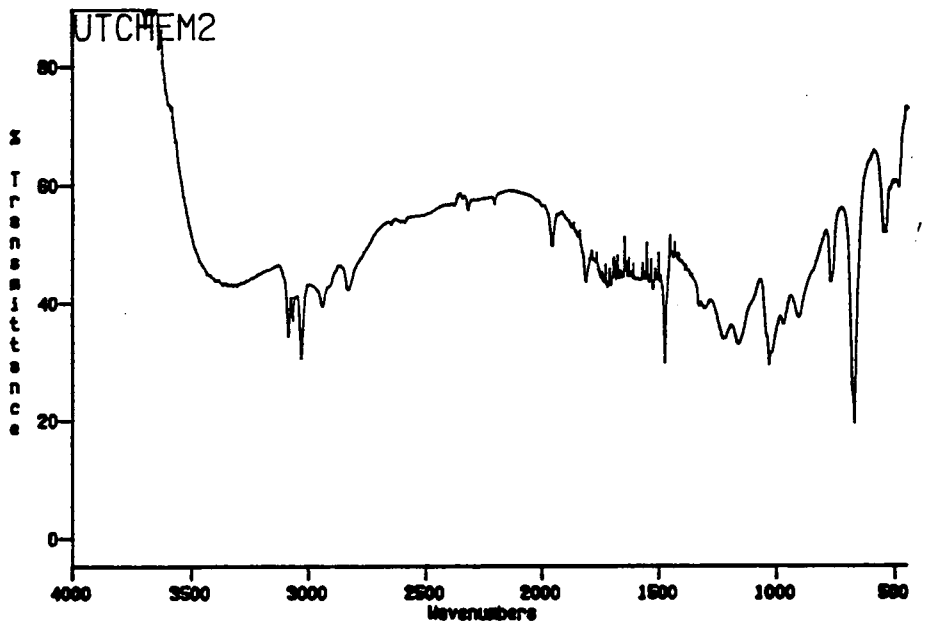


FIGURE 58. FTIR 58. Subtracted methanesulfonic acid. 9TB-BM (figure 49) with a different transmittance scale.

-There is also S=O stretching at 1165-1150 cm^{-1}. A peak at 1161 cm^{-1} was experimentally obtained.

-The stretching vibrations assigned to C-S linkage occur at about 700-600 cm^{-1}. Experimentally a peak at 677 cm^{-1} was obtained and it is probably due to this vibration.[29]

-For methyl group joined to sulfur, the asymmetric vibration appears at 1440-1415 cm^{-1} and the symmetric one at 1330-1290 cm^{-1}. Those peaks in the spectrum could be the peaks at 1481, 1322 or 1218 cm^{-1}.

-Peaks at 1960 and 1816 cm^{-1} are overtone bands from aromatic compounds. Other small peaks comes from either benzene or methanol.

Mix. (See Figure 59.) The interaction between aniline and methanesulfonic acid (1 meq. each) is very strong. Originally, the two single compounds are solutions and immediately form very shiny, white crystals when they are placed together. The main characteristics of this spectrum are the following:

-There is neither N-H stretching from aniline (3361 cm^{-1}) nor the broad band of O-H stretching from methanesulfonic acid (3333 cm^{-1}). Instead of those bands, there is a new peak at 2638 cm^{-1} that could correspond to a transfer of proton from -OH (in methanesulfonic acid) to $-NH_2$ (in aniline) forming the anilinium ion.

-The NH_3^+ stretching yields a broad band between 3000 and

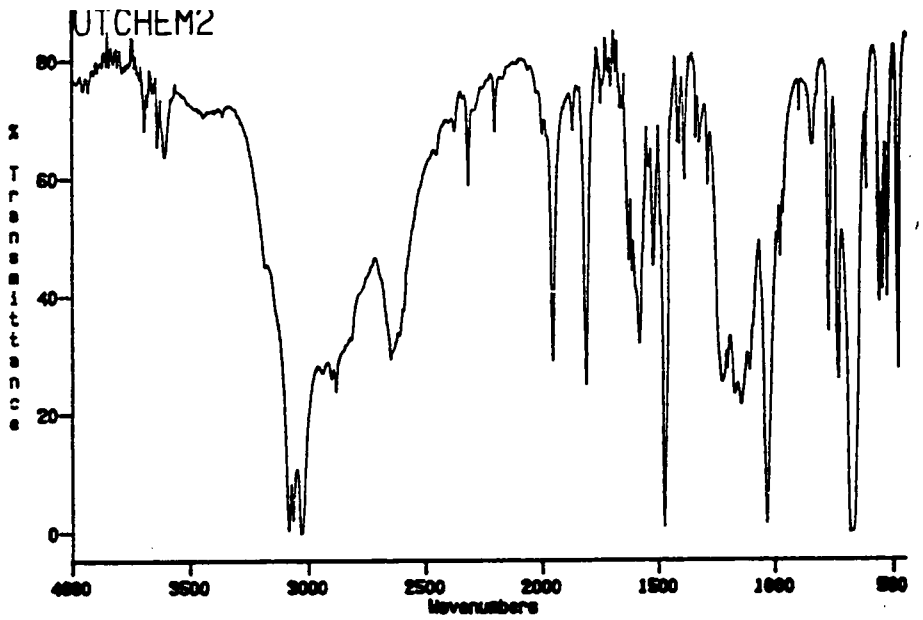


FIGURE 59. FTIR 59. Subtracted aniline : MSA mix (1/1). Subtracted solid portion of 1/1 (figure 53).

2600 cm^{-1}. Multiple combination and overtone bands extend the absorption to about 2000 cm^{-1}. This overtone shows a prominent band near 2222-2000 cm^{-1} assigned to the combination of asymmetric NH_3^+ bending and torsional oscillation of NH_3^+ group. Two peaks at 2322 and 2212 cm^{-1} were experimentally obtained.[29]

-A fairly strong symmetric NH_3^+ bending band appears close to 1550-1485 cm^{-1}. This frequency could probably be the peak at 1525 cm^{-1} in the mix spectrum. Asymmetric bending is approaching the 1660-1610 cm^{-1} range. There is a band at 1598 cm^{-1} that could be assigned to this vibration. There is no clear N-H bending. The broad band combines all. There is a strong peak at 1477 cm^{-1} that is due to C-C stretching. The peak frequency in the mixture spectrum changed in comparison to the frequency in the two single compounds.

-The C-C ring bending in aniline (680 cm^{-1}) and the C-S stretching in methanesulfonic acid (677 cm^{-1}) form the stronger band at 677 cm^{-1} in the mix spectrum.

-The broad band that appears at about 800-666 cm^{-1} for N-H wagging in the aniline spectrum does not appear in the mix spectrum.

-Other peaks in the mix are either from aniline, methane sulfonic acid, or both compounds. Among them:

C-N stretching appears at 1036 cm^{-1}.

C-H aromatic stretching between 3092 and 3031 cm^{-1}.[26,29]

C-H stretching from methyl group at 2893 cm^{-1}.
S=O stretching and C-H in plane bend are combined in the band at about 1200 cm^{-1}.
C-H aromatic out of plane ring bending at 738 cm^{-1}.
C-C bending in and out of plane with two peaks between 580 and 420 cm^{-1}.

Aniline : Phenyl phosphinic acid. The interaction among these two compounds was analyzed with the same solvent, benzene-methanol in a ratio 75/25 (BM-75), and with the same concentrations in the original solutions as studied in the first interaction aniline : methanesulfonic acid. Nine dilutions with ratios 1/0, 5/1, 2/1, 1.25/1, 1/1, 1/1.25, 1/2, 1/5, 0/1 (milliequivalents of aniline : milliequivalents of phenyl phosphinic acid) were prepared from the 4N BM-75 solution of aniline and the 0.8N BM-75 solution of phenyl phosphinic acid.

There is no solid formation when aniline and phenyl phosphinic acid are placed together. This is the main difference with the interaction studied earlier: the nine dilutions remain liquid.

After BM-75 subtraction, the nine spectra were analyzed to comprehend how aniline and phenyl phosphinic acid (PPA) interact and determine the type of bond formed among them:

*Figure 60. The subtracted (after solvent subtraction)

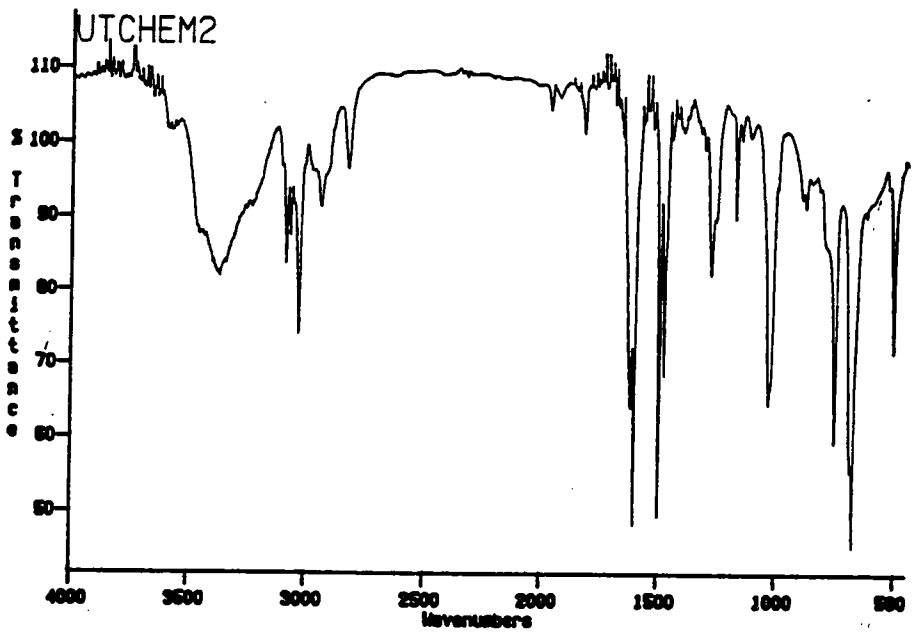


FIGURE 60. FTIR 60. Aniline : Phenyl phosphinic acid (PPA). Subtracted ratio 1/0. Aniline spectrum after solvent subtraction. (See figure 57.)

aniline spectrum is displayed in this figure and it looks very similar to the spectrum obtained for the former interaction.

*Figure 61. Aniline is still present because of its excess and the O-H extends to 2500 cm^{-1}.

*Figure 62. The broad band extends to nearby 2000 cm^{-1}. The peak at about 2300 cm^{-1} is due to P-H stretching from phenyl phosphinic acid (PPA).

*Figure 63. The band at 2600 cm^{-1} becomes stronger and the peak at 1600 cm^{-1} (due to N-H bending from aniline) changes its shape.

*Figure 64. At this ratio, the interaction between the compounds is complete. The configuration of the P-H stretching peak is also changed.

*Figure 65. The interaction becomes weaker than in Figure 64.

*Figure 66. The spectrum shows differences in the 1250-1000 cm^{-1} range presumably due to the PPA excess.

*Figure 67. The interaction is now really weak, as shown in spectrum and comparison with the previous spectra.

*Figure 68. This spectrum corresponds to phenyl phosphinic acid. Note that the bands surrounding the P-H stretching frequency at about 2300 cm^{-1} have already left.

The bond obtained in this analysis appears to be less strong than the force between aniline and methanesulfonic acid. The link is complete when it is at a ratio of milli-

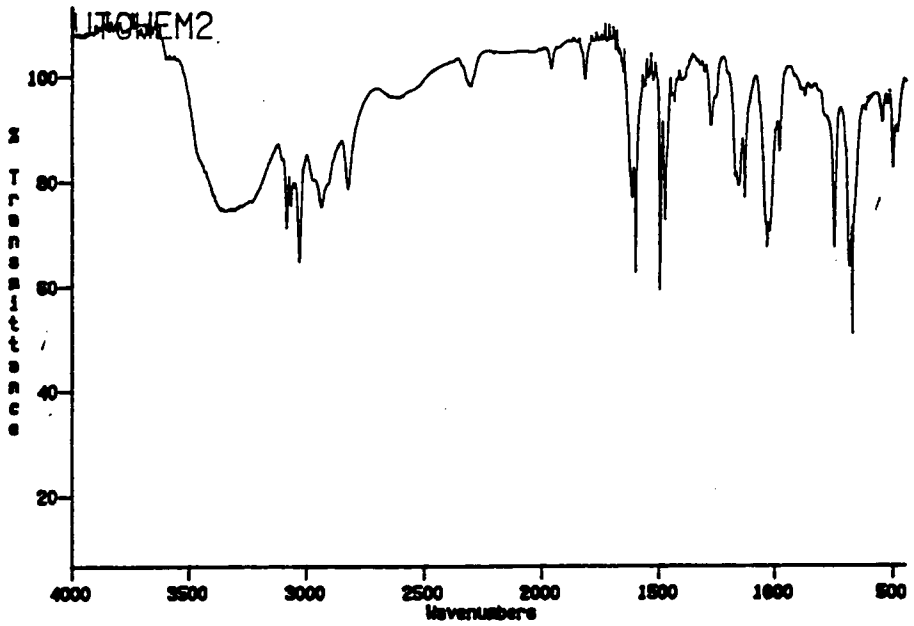


FIGURE 61. FTIR 61. Aniline/PPA. Subtracted ratio 5/1. There is no solid formation.

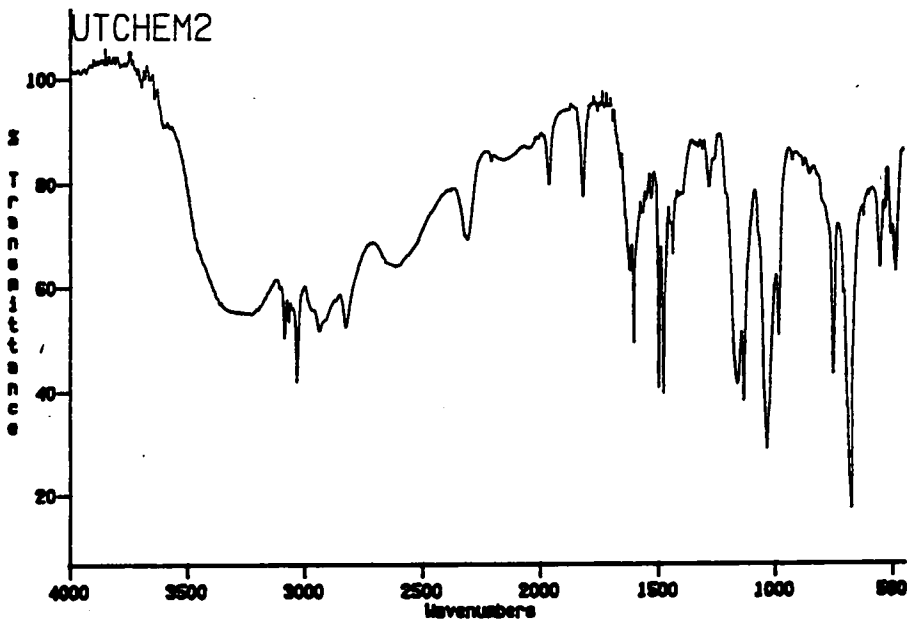


FIGURE 62. FTIR 62. Aniline/PPA. Subtracted ratio 2/1. The broad band extends to nearby 2000 cm^{-1}.

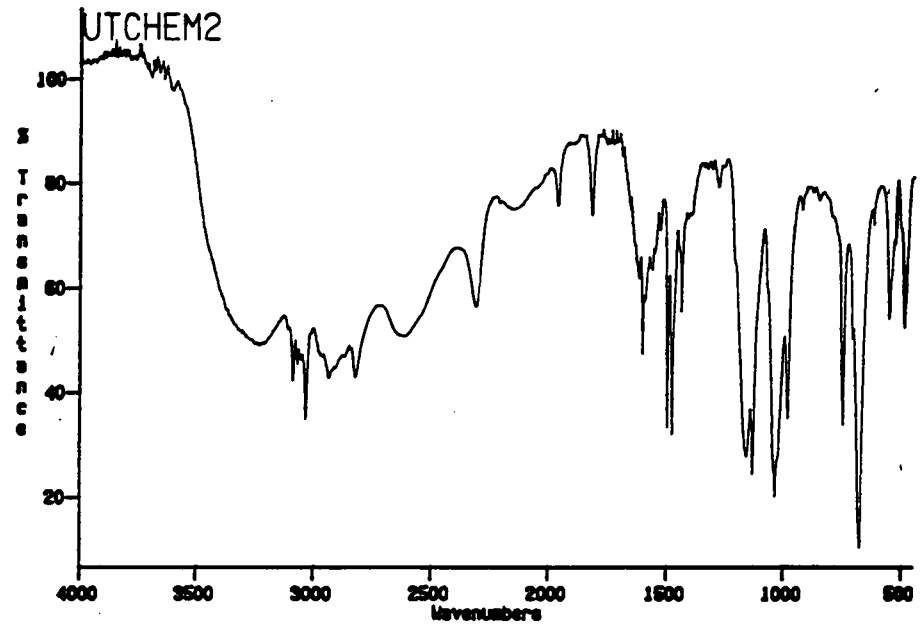


FIGURE 63. FTIR 63. Aniline/PPA. Subtracted ratio 1.25/1. The band at 2600 cm^{-1} becomes stronger than in the previous spectra.

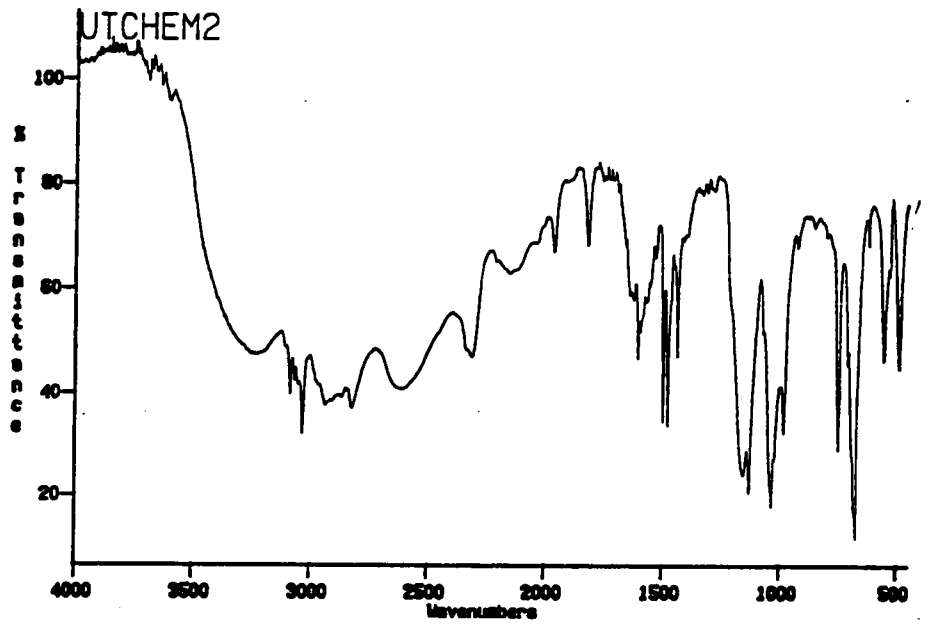


FIGURE 64. FTIR 64. Aniline/PPA. Subtracted ratio 1/1. The interaction appears to be complete at this ratio.

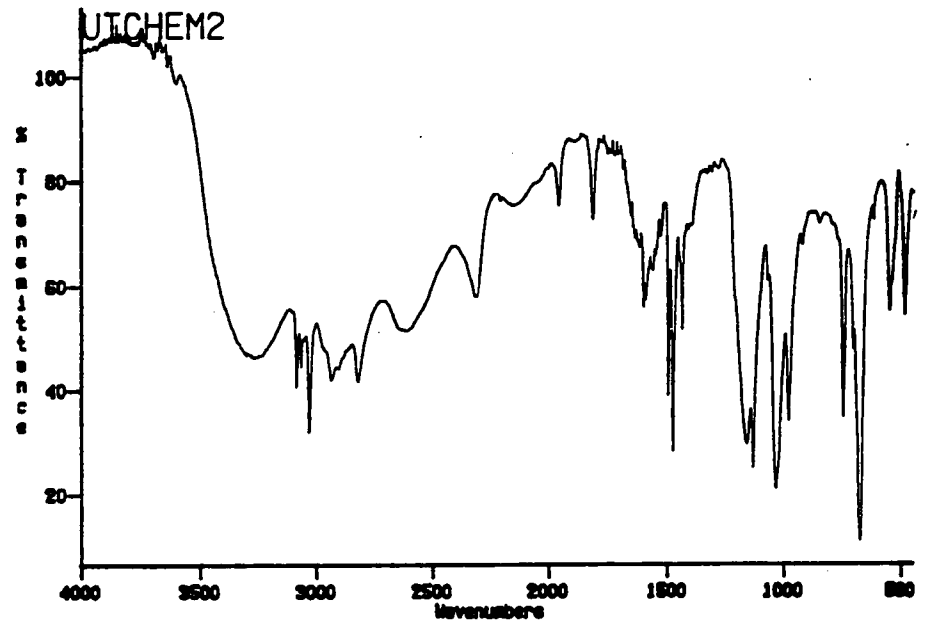


FIGURE 65. FTIR 65. Aniline/PPA. Subtracted ratio 1/1.25.

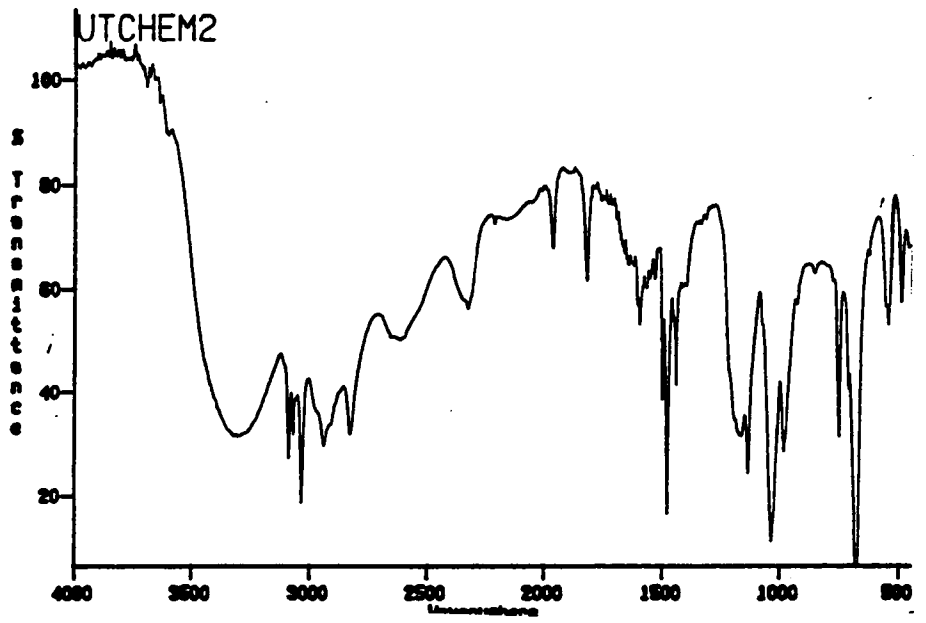


FIGURE 66. FTIR 66. Aniline/PPA. Subtracted ratio 1/2.

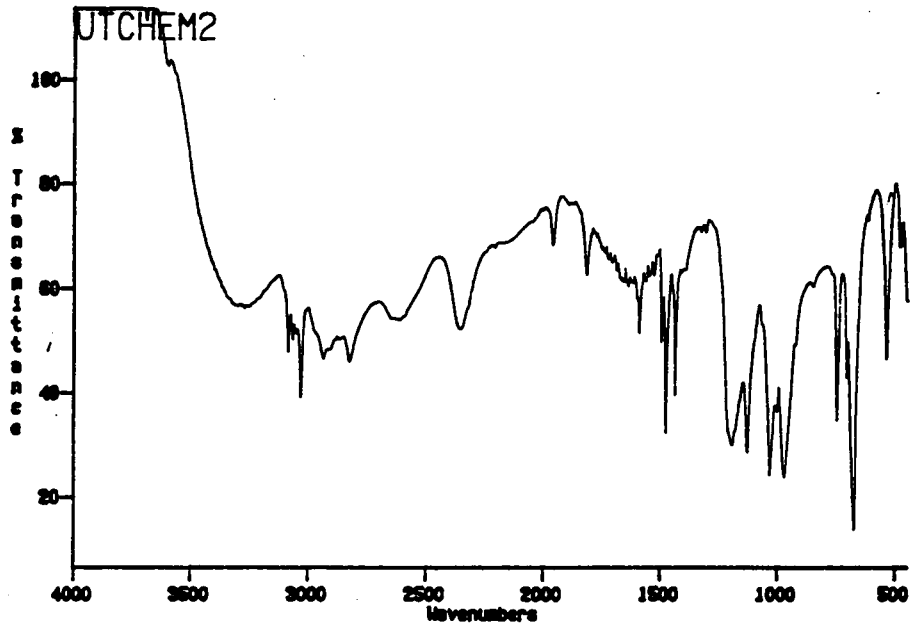


FIGURE 67. FTIR 67. Aniline/PPA. Subtracted ratio 1/5. The band at about 2600 cm^{-1} becomes smaller than in the previous spectrum.

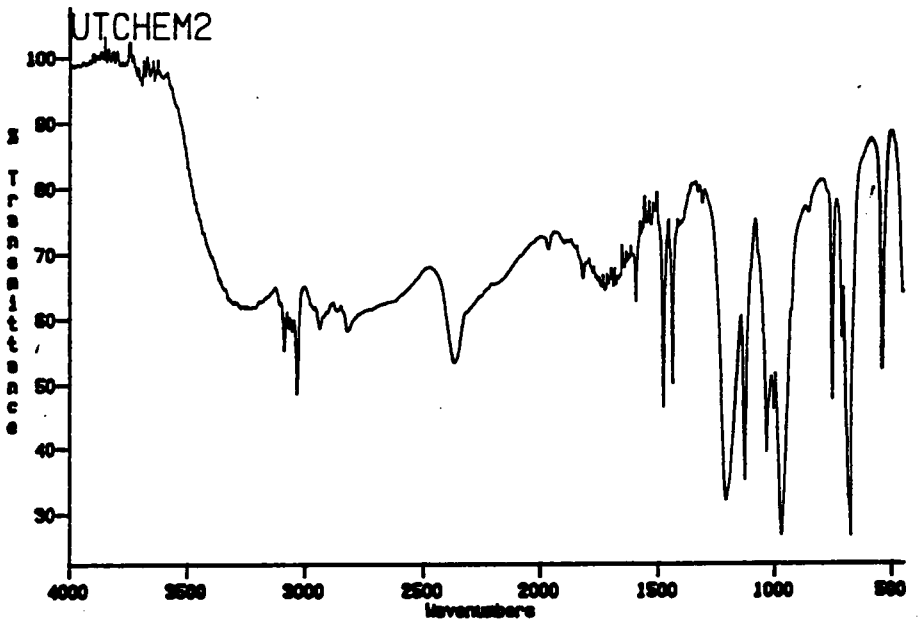


FIGURE 68. FTIR 68. Aniline/PPA. Subtracted ratio 0/1. Phenyl phosphinic acid spectrum.

equivalent of aniline : milliequivalent of PPA.

Aniline. (See Figure 60.) It is an aromatic compound whose peak analysis was completed previously. The solvent subtraction displays a better spectrum for aniline. All the peaks show a tiny difference with regard to wavenumbers if Figures 57 and 60 are compared; therefore, there is reproducibility in the subtraction technique.

Some of the frequencies shown in the spectrum are the the following:

-The N-H stretching at 3458 and 3235 cm^{-1}. Band at 3372 cm^{-1} is due to methanol. The experiment corroborates low resolution for this region in which methanol absorbs infrared radiation strongly.

-The C-H aromatic stretching at about 3100-3000 cm^{-1}, and the C-H stretching from methyl groups (solvent) at 2939 cm^{-1} and 2829 cm^{-1}.[26,29]

-The N-H bending at 1628 cm^{-1} and a weak band at 1276 cm^{-1}.

-The C-C stretching in the ring at 1602, 1499, and 1482 cm^{-1}, and C-C bending in the ring at 678 cm^{-1}.

-The C-N stretching at 1028 cm^{-1}.

-The C-H out of plane ring bending at 759 cm^{-1} and C-H in plane bending at 1176 cm^{-1}.

-A broad band at about 800-666 cm^{-1} which corresponds to N-H wagging.

-In plane and out of plane ring deformation for benzene

derivatives display two bands between 580 and 420 cm^{-1}. A peak at 510 cm^{-1} is experimentally obtained.
-Peaks at 1967 and 1820 cm^{-1} are overtone bands produced by aromatic compounds.

Phenyl Phosphinic acid. (See Figure 68.) It is an aromatic compound with molecular formula $C_6H_5P(O)(OH)H$. Phenyl phosphinic acid is an irritant compound and it is not as strong as methanesulfonic acid.

The most important frequencies shown by the spectrum of phenyl phosphinic acid are the following:
-Broad intermolecular hydrogen bond from O-H stretching at 3292 cm^{-1}.
-The C-H aromatic stretching at about 3100-3000 cm^{-1}. It is possible to distinguish two peaks at 2939 and 2819 cm^{-1} that are due to C-H stretching from methyl groups (probably BM-75 remaining).[29]
-The C-H in plane bending at 1131 cm^{-1} and the C-H out of plane ring bending at 735 cm^{-1}.
-The P-H stretching at 2366 cm^{-1}.
-The C-C stretching in the ring at 1595, 1483 and 1436 cm^{-1}.
-The C-C bend ring at 680 cm^{-1}.
-The P=O stretching at 1204 cm^{-1} (very strong peak).[26]
-The P-OH stretching at about 1000 cm^{-1} (strong band).
The peak at 537 cm^{-1} could be one of the two peaks that correspond to in and out of plane ring deformation for

benzene derivatives.

Mix. (See Figure 64.) When phenyl phosphinic acid and aniline (1 meq. each) are placed together, there is no visible change. The mixture remains liquid; however, some changes are observed in the spectrum.

Some of the frequencies that appear in the spectrum are the following:

-The O-H stretching at 3293 cm^{-1}.

-The C-H aromatic stretching and C-H stretching from methyl group (solvent) at the 3100-2850 cm^{-1} range.[26,29]

There is a shift for P-H stretching, from 2366 cm^{-1} (PPA) to 2324 cm^{-1} (mix). There are two new bands at 2601 cm^{-1} and 2142 cm^{-1} that could be related to a hydrogen bond between the two compounds. The hydrogen bond lowers the stretching frequencies. There is no salt formation as in the first study done with aniline and methanesulfonic acid.

The band for the N-H bending is not clear. It is broad, very weak and at higher frequency (1632 cm^{-1}) than aniline (1628 cm^{-1}). The hydrogen bond raises the bending frequencies.

There is no N-H wagging at about 800-666 cm^{-1} (see aniline).

Peaks below 1600 cm^{-1} are a combination of both compounds or come from either aniline or phenyl phosphinic acid.

In and out of plane ring deformation for benzene derivatives display two peaks between 580 and 420 cm^{-1}. Because of the hydrogen bond, the frequencies were probably raised; there-

fore, two peaks can be viewed at 552 and 485 cm^{-1}.[26]
The C-C bending in the ring frequency was also increased (strong peak at 682 cm^{-1} in the mix, 678 cm^{-1} in aniline and 680 cm^{-1} in phenyl phosphinic acid).
The P=O stretching frequency, the strong peak at 1204 cm^{-1} in phenyl phosphinic acid, was lowered. A band is displayed at 1160 cm^{-1}.
Peaks between 1600 and 1438 cm^{-1} are due to C-C stretching in the ring for both compounds.
The region between 1100 and 900 cm^{-1} is a combination in the mix of C-N stretching from aniline, P-OH stretching from phenyl phosphinic acid, and C-H in plane bending.[26,29] When the spectra are compared, there are some differences which may be due to the hydrogen bond formation.

Aniline : Benzoic acid. The interaction within aniline and benzoic acid was studied with BM-75 as the solvent and with a 4N BM-75 solution of aniline and a 0.8N BM-75 solution of benzoic acid. Only three dilutions were prepared with ratios 1/0, 1/1, 0/1 (milliequivalents of aniline : milliequivalents of benzoic acid). After solvent subtraction the following spectra were analyzed:

Aniline. (See Figure 69.) After being analyzed, its interaction with a very strong acid, such as methanesulfonic acid and with a compound of medium acidity, such as phenyl phos-

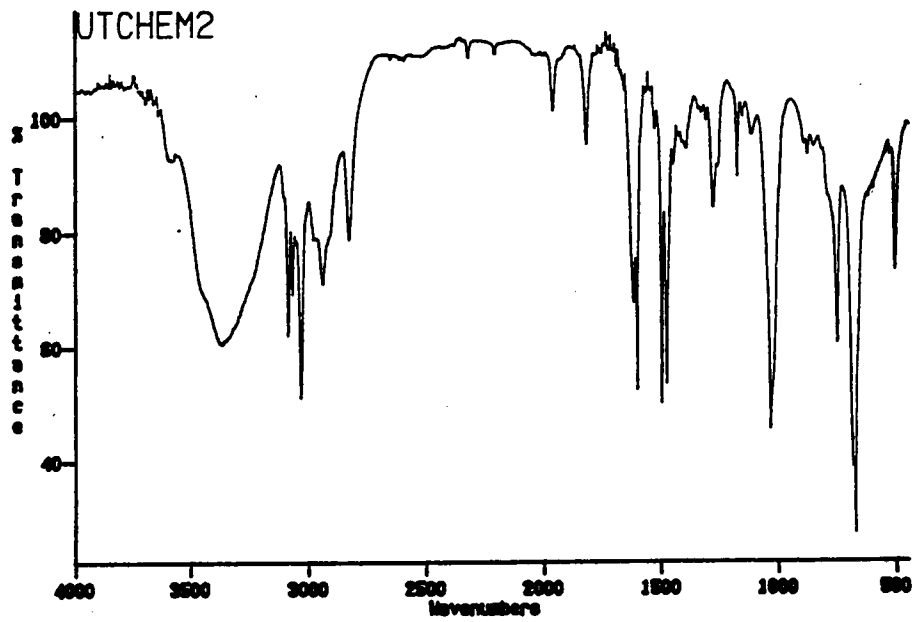


FIGURE 69. FTIR 69. Subtracted aniline. Aniline spectrum after BM-75 subtraction (S.F.= 0.5). Ratio 1/0 in aniline : benzoic acid interaction.

phinic acid, the study was done with benzoic acid, the weakest of the three acid compounds.

Comparing the spectra (see figures 57, 60, and 69), the three look alike. As a result, there is reproducibility in the subtraction as told previously.

Benzoic Acid. (See Figure 70.) It is an aromatic, very irritant compound with formula C_6H_5COOH.

Benzoic acid is an organic compound that dimerizes. There is a broad band with center at 3363 cm^{-1} that corresponds to O-H···O intermolecular hydrogen bond. There is no free O-H which usually occurs at about 3600-3580 cm^{-1}. Carboxylic acid dimers display very broad, intense O-H stretching absorption in the region 3000-2500 cm^{-1}.

Other particular peaks analyzed for the compound are the following:

-The C-H aromatic stretching appears at 3090, 3069, 3031 cm^{-1} and the C-H stretching from methyl groups (methanol in solvent) appears at 2942 and 2829 cm^{-1}.[26,29]

-The two bands at 2638 and 2517 cm^{-1} might be product of the dimerization. Overtone bands appear between 2000 and 1800 cm^{-1} for aromatic compounds.

-A very strong peak at 1703 cm^{-1} indicates the C=O stretching. The normal frequency is usually at 1715 cm^{-1}; in this case, the conjugation with the phenyl group causes the absorption at a lower wavenumber.

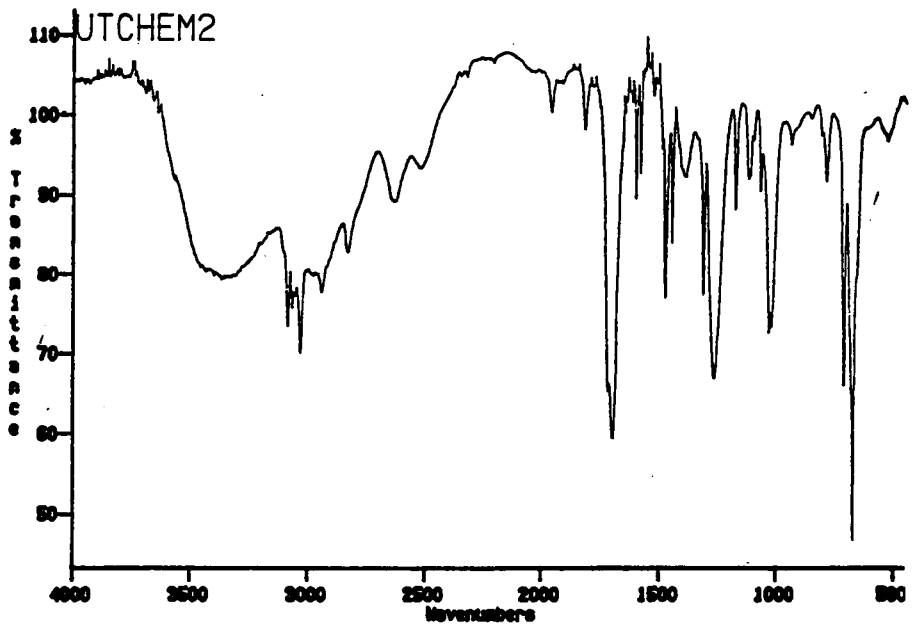


FIGURE 70. FTIR 70. Subtracted benzoic acid. Benzoic acid spectrum after BM-75 subtraction (S.F.= 0.6). Ratio 0/1 in aniline : benzoic acid interaction.

-The C-C stretching in the ring is displayed at 1605, 1482, and 1449 cm^{-1}, and the C-C bending in the ring is displayed at 674 cm^{-1}.

-The small band at 1397 cm^{-1}, the sharp peak at 1320 cm^{-1}, the strong band at 1268 cm^{-1} and the small peak at 1176 cm^{-1} could be due to combination between O-H bending and C-O stretching. The latter produces a strong band in the 1260-1000 cm^{-1} region for alcohols and phenols.[26,29]

Dimeric carboxylic acids disclose a broad, medium intensity band near 920 cm^{-1}, due to out of plane bending of the bonded O-H. It could be the band shown at 1027 cm^{-1} in this spectrum. Other frequencies displayed in the spectrum are the following: C-H in plane bend at 1120 cm^{-1}, combined with C-O stretching and O-H bending. At 714 cm^{-1}, there is also a peak that corresponds to C-H aromatic out of plane ring bend.

Mix. (See Figure 71.) The combination between aniline and benzoic acid does not have visible change (as in interaction with phenyl phosphinic acid). The mix spectrum has small variations compared to the two single compounds indicating that there is a very weak interaction within the benzoic acid and aniline.

The frequencies in the mix spectrum are the following:

-The O-H bonded changes in the 3300 cm^{-1} region (see aniline and benzoic acid). This is the range for the N-H stretching

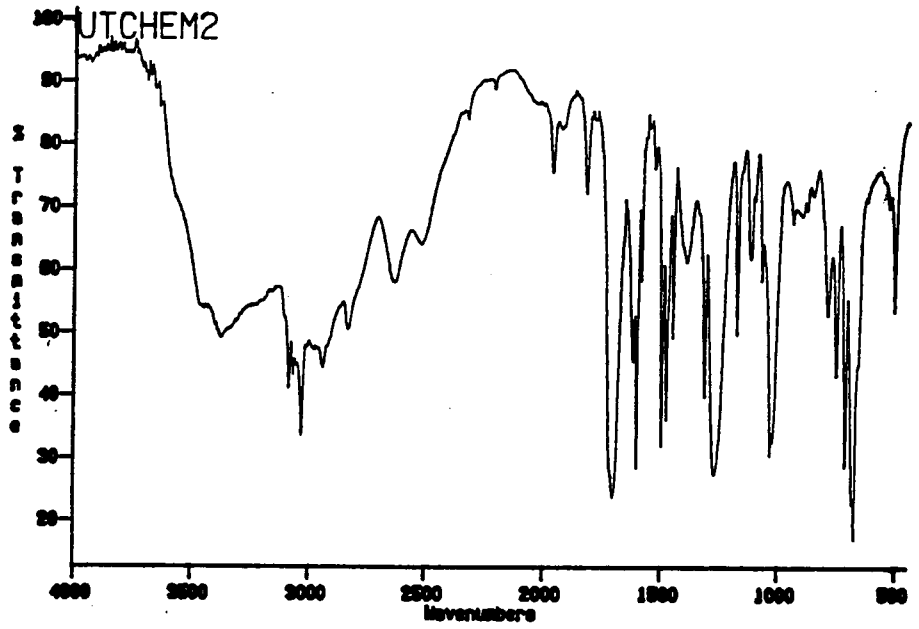


FIGURE 71. FTIR 71. Subtracted mix. Mix spectrum after BM-75 subtraction (S.F.= 0.6). Ratio 1/1 in aniline : benzoic acid interaction.

from aniline and the O-H intermolecular bond of the dimeric acid.

-The C-H aromatic stretching occurs at about 3100-3000 cm^{-1}, and the C-H stretching of the methyl groups appears at 2943 and 2830 cm^{-1}.

-The combination of bands at 2637 and 2519 cm^{-1} is stronger than that of benzoic acid; consequently, this could prove a weak hydrogen bond between aniline and benzoic acid.

-The N-H wagging in the aniline spectrum is a broad band (800-666 cm^{-1}) that decreases in the mix spectrum.

The other peaks are either from aniline or benzoic acid (1700-500 cm^{-1}).[26,29]

Phenol : Phenyl phosphinic acid. This study was performed to compare the force of the interaction between phenol and phenyl phosphinic acid with the three interactions investigated earlier. The solvent was BM-75, and 0.8N BM-75 solutions of phenol and phenyl phosphinic acid were used. Three dilutions with ratios 1/0, 1/1 and 0/1 were prepared.

Phenol. (See Figure 72.) It is a highly toxic, corrosive and aromatic compound with formula C_6H_5OH.

The principal bands in the spectrum are the following:

-The broad band at 3288 cm^{-1} corresponds to intermolecular O-H bonded (methanol from solvent is affecting this range). There is also a small peak at 3567 cm^{-1} that could corre-

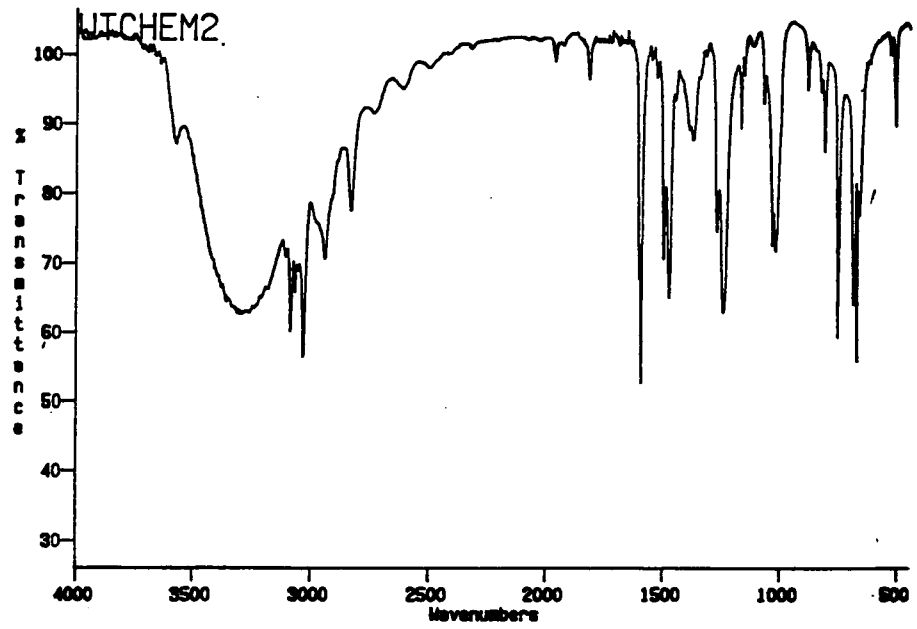


FIGURE 72. FTIR 72. Subtracted phenol. Phenol spectrum after BM-75 subtraction (S.F.= 0.8). Ratio 1/0 in phenol : PPA interaction.

spond to the unbonded or "free" O-H.

-All peaks between 3100 and 2800 cm^{-1} are due to the C-H stretching from either phenol or methyl groups of solvent.

-The little peaks in the 2800-2500 cm^{-1} could also be due to hydrogen bond extension, but it is difficult to believe it forms in a high extension.

-The C-C stretching in the ring is displayed at 1605, 1501, and 1477 cm^{-1} and C-C bending at 667 cm^{-1}.[26,29]

-The range at about 1250 cm^{-1} is a combination of O-H bend, C-O stretching and C-H in plane bend.

Phenyl phosphinic acid. (See Figure 73.) This spectrum can be compared with Figure 68 with very small differences due to the solvent subtraction.

Mix. (See Figure 74.) The interaction between phenol and phenyl phosphinic acid is really weak. The little peak related to unbonded O-H in phenol changes in the mix spectrum (see phenol spectrum). The small peaks in the 2800-2500 cm^{-1} presumably refer to a very weak hydrogen bond. The other peaks in the mix spectrum are a combination of the two single compounds. For example, the band near 1213 cm^{-1} is an addition of P=O stretch from PPA (1210 cm^{-1}) to the combination of O-H bending and C-O stretching from phenol (1266, 1237 cm^{-1}). The band at about 3300 cm^{-1} has a very small shift to a lower frequency than in the two single

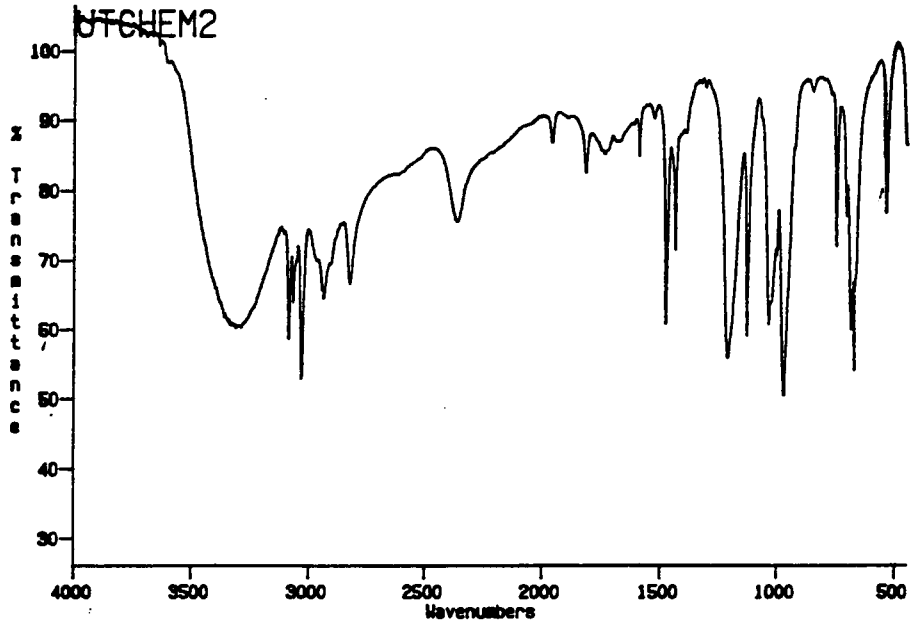


FIGURE 73. FTIR 73. Subtracted phenyl phosphinic acid. PPA spectrum after BM-75 subtraction (S.F.= 0.6). Ratio 0/1 in phenol : PPA interaction.

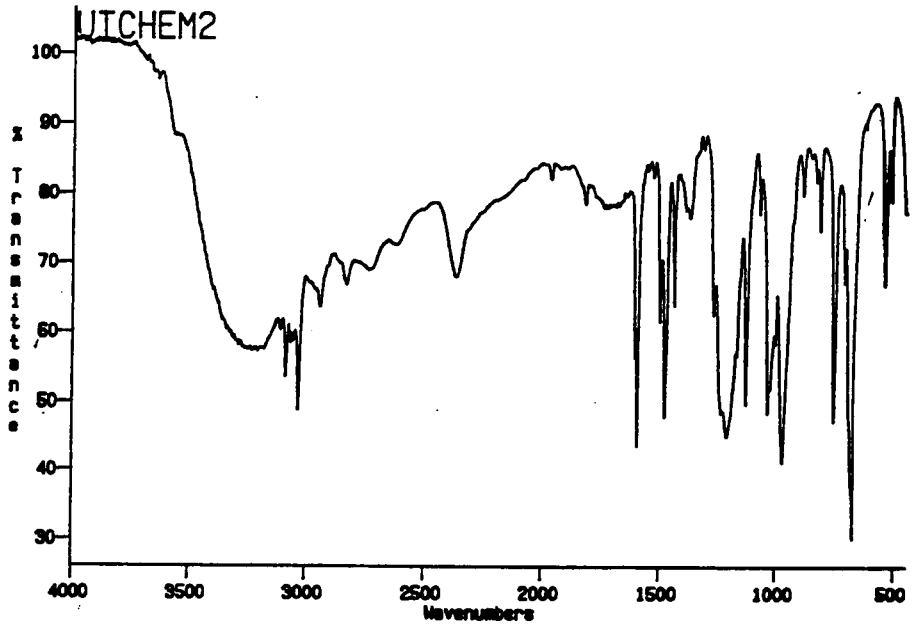


FIGURE 74. FTIR 74. Subtracted mix. Mix spectrum after BM-75 subtraction (S.F.= 0.7). Ratio 1/1 in phenol : PPA interaction.

compounds.

* Polymer Interactions.

The study was carried out with polymeric sulfonic acid and polymeric phosphinic acid. The interaction was done with aniline for a 17-hour period at a ratio of a milliequivalent of resin to a milliequivalent of aniline. After the reaction, the solvent was evaporated and a KBr pellet was made to record the FTIR spectra of the solid samples.

Aniline : Polymeric sulfonic acid. For this investigation, golden beads of the resin and a 4N BM-75 solution of aniline were used, as well as methanol and BM-75 for the solvent exchange. These resins are kept in deionized water; otherwise, they collapse and no reaction is possible.

Aniline. (See Figure 69.) For this study, aniline is compared through the spectrum obtained in the aniline : benzoic acid interaction.

Polymeric sulfonic acid. (See Figure 75.) This resin is formed when divinylbenzene crosslinked styrene gel copolymer beads are placed in contact with concentrated sulfuric acid, dichloroethane (a swelling solvent) and water in a three-neck round bottom flask equipped with an overhead stirrer, condenser, and thermometer. The

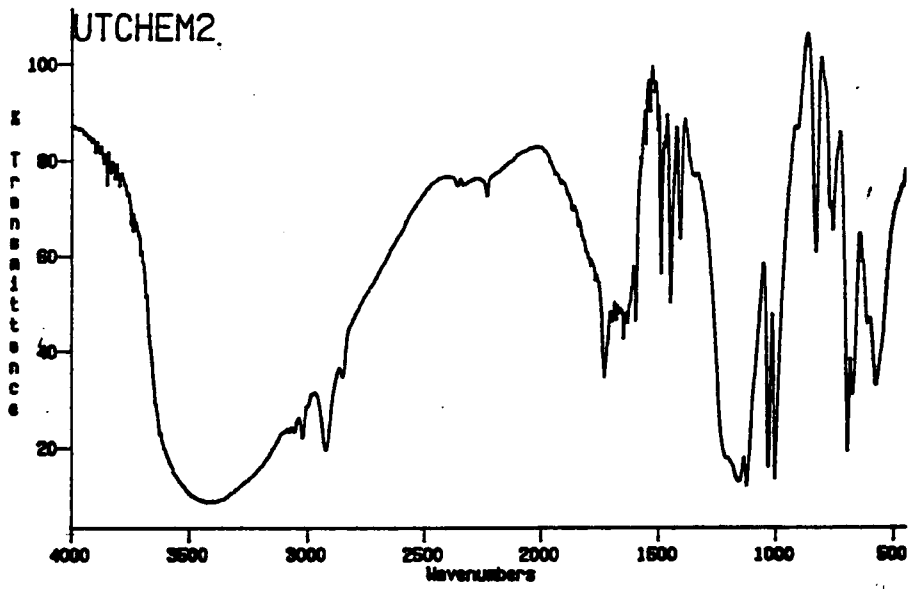


FIGURE 75. FTIR 75. Polymeric sulfonic acid spectrum. (KBr pellet.)

reaction mixture is stirred at room temperature for 15 min, heated to 130°C over a period of 3h, held at 130°C for 15 min, and then cooled to 110°C. The reaction is slowly quenched by the dropwise addition of water with subsequent siphoning of the water from the reaction flask. The operation is repeated until the reaction mixture maintains room temperature. The resin is then washed and conditioned with elutions of water, NaOH, HCl, and water.[17]

The resin spectrum displays strong bands:

-The very broad, strong band at 3381 cm^{-1} corresponds to O-H (intermolecular or intramolecular) bonded.

-The peaks at 3086, 3066, and 3030 cm^{-1} are due to C-H aromatic stretching, and the peaks at 2927 (strong) and 2855 cm^{-1} are due to C-H stretching from the methylene groups in the backbone of the polymer chain (vinyl groups).[26,29]

-The C-C stretching in the ring appears at 1599, 1496, and 1450 cm^{-1} and the C-C bend ring is shown at 676 cm^{-1}.

-The stretching vibrations assigned to the C-S link occur at 700-600 cm^{-1}. A sharp peak at 700 cm^{-1} was obtained.

-The strong band at 1180 cm^{-1} could correspond to S=O stretching, which for the sulfonic acid group is about 1350-1342, 1165-1150 cm^{-1}. There is a small peak (without resolution) at 1334 cm^{-1}.[29]

-The O-H in plane bending comes into view at 1420-1330 cm^{-1}. There is a peak at 1411 cm^{-1} which could be assigned to this bond movement.

-The C-H in plane bending takes place at 1208 cm^{-1} (in the broad band with center at 1180 cm^{-1}).
-The C-H stretching out of plane ring appears at 761 cm^{-1}. There is a peak at 832 cm^{-1} which is due to C-H out of plane deformation for para-substituted benzene derivatives. In the polymer, the benzene ring is joined to the sulfonic group on the opposite side of the backbone.[26]

Mix. (See Figure 76.) When polymeric sulfonic acid and aniline are deposited together, a very powerful interaction takes place. The color of the beads changes to a very light golden color. In addition, a broad band (no resolution) from 3600 to 2000 cm^{-1} is displayed in the mix spectrum. The band includes many frequencies of each single compound and some features of the interaction. The main difference in the mix (already seen in other interactions such as aniline with methanesulfonic acid), is the band shown at about 2600 cm^{-1}. The band also includes the N-H stretching from aniline or the O-H stretching from the resin (3455 cm^{-1}), the C-H aromatic stretching from both compounds (3100-3000 cm^{-1}), the C-H from methylene groups in the polymer backbone (displayed at about 3000-2800 cm-1), and the stretching of NH_3^+; this could be the same result of the interaction in methanesulfonic acid / aniline: the formation of the anilinium ion.[29]
There is a new, strong band at about 1500-1700 cm^{-1} that is

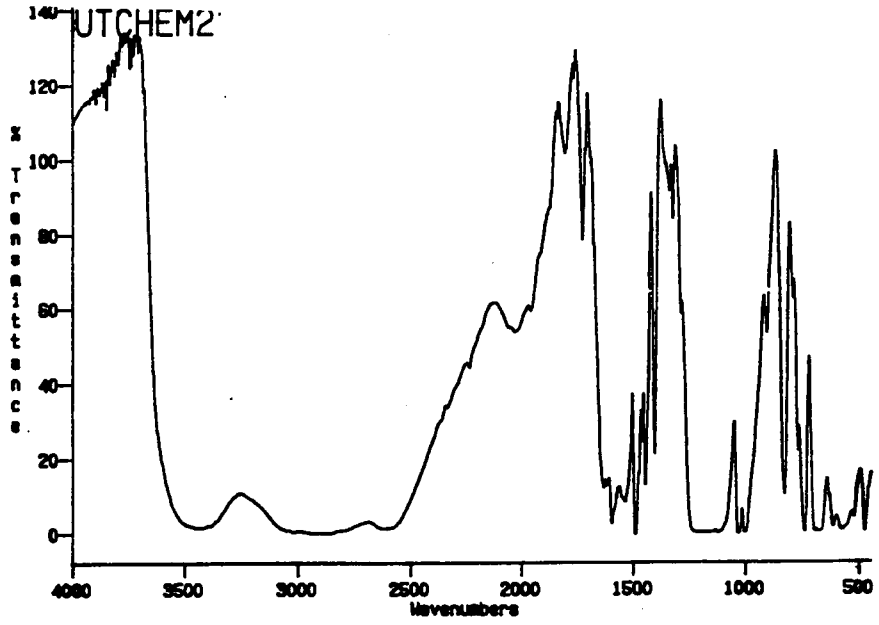


FIGURE 76. FTIR 76. Aniline : Polymeric sulfonic acid mix. Spectrum recorded with a KBr pellet.

possibly the result of the symmetric NH_3^+ bending (strong band at about 1500-1550 cm^{-1}) and the asymmetric NH_3^+ bending (band at about 1660-1610 cm^{-1}). These bands are seen when the interaction within aniline and methanesulfonic acid is studied.

Other peaks are related to C-C stretching in the ring which are exhibited at 1599, 1497, and 1448 cm^{-1}. The C-N stretching from aniline and the S=O stretching from the resin are in the 1200-1000 cm^{-1} region. The peaks at 800-500 cm^{-1} are due to the C-S stretching from the polymeric sulfonic acid (band at about 700 cm^{-1}), and the aromatic compounds bending vibrations, and out of plane and in plane ring deformations.[26,29]

Aniline : Polymeric phosphinic acid. In this study, snow white beads of polymeric phosphinic acid and a 4N BM-75 solution of aniline were used as well as BM-75 and methanol for the solvent exchange.

Aniline. (See Figure 69.) In this study (as in the aniline : polymeric sulfonic acid study), the aniline spectrum obtained in its interaction with benzoic acid was used to compare the single compound with the mix.

Polymeric phosphinic acid. (See Figure 77.) Electrophilic aromatic substitution by the PCl_3 on the phenyl rings of the

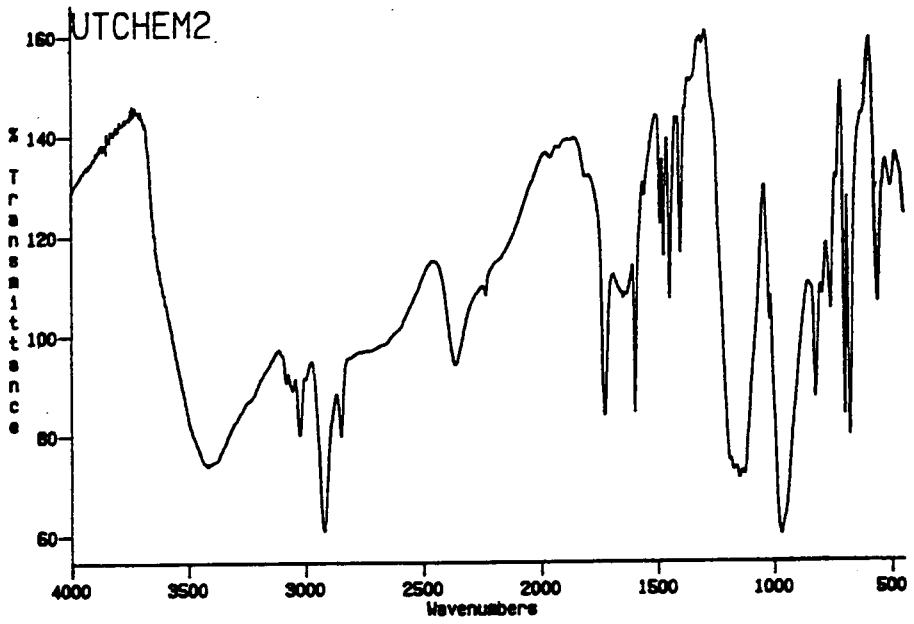


FIGURE 77. FTIR 77. Polymeric phosphinic acid spectrum. (KBr pellet.)

2% divinylbenzene crosslinked polystyrene gel beads is catalyzed by $AlCl_3$ to form the phosphinic resin. The reaction goes to completion upon refluxing at 73°C for 4 hours. Subsequent hydrolysis of the chlorophosphine intermediate leads to the isolation of the phosphinic resin.[1]

The resin spectrum shows:

-The broad band at 3398 cm^{-1} is due to O-H bonding and the peaks at about 3100-3000 cm^{-1} are due to C-H aromatic stretching.

-The strong peak at 2924 cm^{-1} and the weaker one at 2850 cm^{-1} correspond to C-H asymmetric and symmetric stretching of methylene groups from the polymer chain.[29]

-The peak at 2362 cm^{-1} is due to P-H stretching.

-The broad band at about 1156 cm^{-1} is a combination of C-H in plane bending (usually at 1208 cm^{-1}) and P=O stretching (generally at 1190 cm^{-1}).

-The C-C stretching, as in other interactions, appears at 1599, 1495, and 1449 cm^{-1}, and the C-C bending appears at 676 cm^{-1}.

O-H in plane bending displays a peak between 1420 and 1330 cm^{-1}. The peak at 1405 cm^{-1} can be attributed to this bond vibration.[26,29]

The strong band that appears at 963 cm^{-1} is due to the P-OH stretching (commonly between 910 and 1040 cm^{-1}). Emerging from that band, there is a sharp peak at 823 cm^{-1} that corresponds to the para-substituted C-H out of plane defor-

mation and another peak at 759 cm^{-1} that can be assigned to the C-H aromatic out of plane ring bend.

Mix. (See Figure 78.) The mixture among aniline and polymeric phosphinic acid produces a new color on the resin beads. From snow white, the beads change to a tan color. According to the spectrum, there is an interaction within them. Hence, it is not as strong as the link between aniline and polymeric sulfonic acid, studied earlier. The most important distinction is the peak at about 2600 cm^{-1}.

The mix spectrum exposes the following bands:

The band at 3367 cm^{-1} (much weaker than in sulfonic resin : aniline mix spectrum) could be assigned to O-H bonding and N-H stretching. The O-H bond extends the absorption up to 2000 cm^{-1} due probably to the hydrogen bond formation amid the two compounds. The peaks at 2602 and 2122 cm^{-1} seem to be the product of this bond. The P-H stretching is at 2324 cm^{-1}. The peaks (no resolution) at 3100-3000 cm^{-1} are due to C-H aromatic stretching and the peaks at 2924 and 2849 cm^{-1} are due to C-H stretching from methylene groups in the polymer chain.[26,29]

The band for N-H bending (1620 cm^{-1} in aniline) is not clear in the mix. The peak at 1599 cm^{-1} is due to C-C stretching with peaks at 1498 and 1449 cm^{-1}.

Bands at lower wavenumbers come from either aniline or the phosphinic resin.

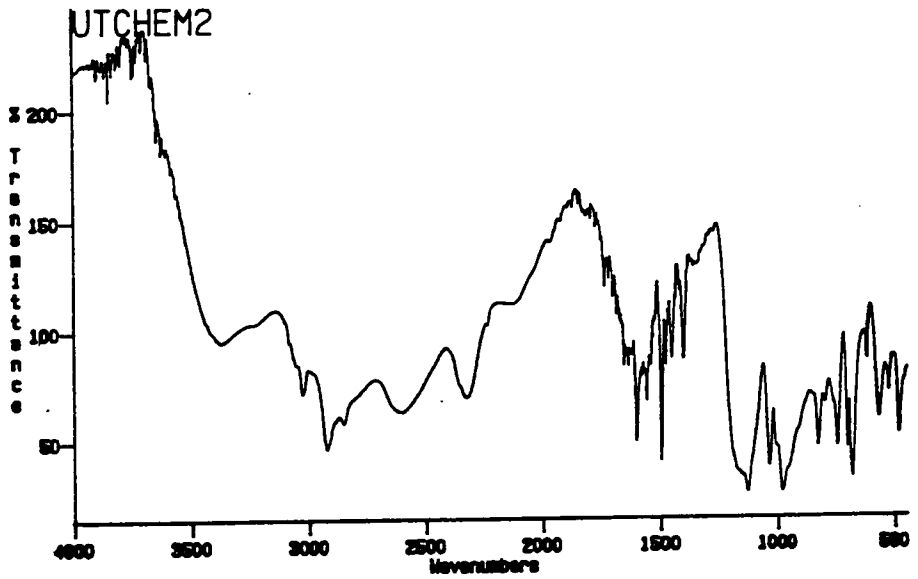


FIGURE 78. FTIR 78. Aniline : polymeric phosphinic acid mix. Spectrum recorded with a KBr pellet.

* Effect of Substituted Anilines on Model Compounds.

To analyze the effect of an electron withdrawer and an electron donor group on the benzene ring of the aniline, two more compounds were analyzed. The interaction of model and polymer compounds was studied with para-methoxyaniline (methoxy is an electron donor group) and meta-chloroaniline (halogens are electron withdrawer groups). The solvent used was benzene-methanol, BM-75, as in former interactions. The new solutions are 1N BM-75 solution of para-methoxyaniline and 4N BM-75 solution of meta-chloroaniline. Three dilutions were prepared for each substituted aniline : model compound research. Those dilution ratios were the following: 1/0, 1/1, 0/1 (milliequivalents of each compound).

para-Methoxyaniline : Methanesulfonic acid. The 1N BM-75 solution of p-methoxyaniline has a brown color. The 0.8N BM-75 solution of methanesulfonic acid is transparent. The two compounds form a brownish white solid when placed together. The three spectra were analyzed to find out if there is a stronger interaction because methoxy is a ring activating group.

p-Methoxyaniline. (See Figure 79.) It is an irritant, aromatic compound, also called p-anisidine. Its formula is $CH_3OC_6H_4NH_2$.

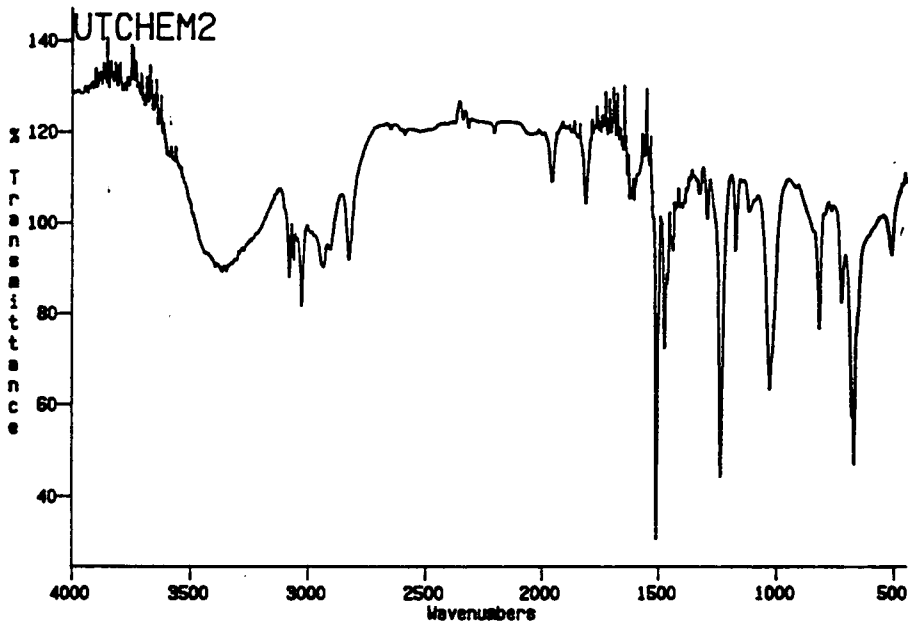


FIGURE 79. FTIR 79. Subtracted p-methoxyaniline. p-Methoxyaniline spectrum after BM-75 subtraction (S.F.= 0.6). Ratio 1/0 in p-methoxyaniline : MSA interaction.

The FTIR spectrum exposes the following peaks:

The broad band at about 3400 cm^{-1} corresponds to N-H stretching (asymmetric and symmetric) with no resolution because of methanol.

-The peaks at 3085, 3062, and 3030 cm^{-1} are due to C-H aromatic stretching. There is little shift compared to aniline because of the methoxy group.

-The peaks at 2943 and 2829 cm^{-1} reflect the C-H stretching vibration from the methyl group.[26,29]

-There are only two peaks at 1504 and 1481 cm^{-1} due to C-C stretching in the ring, and there is one strong peak at 678 cm^{-1} due to C-C bend ring.

-The peak at 1239 cm^{-1} is probably due to C-O stretching. It is not in aniline, and C-O-C in aryl alkyl ethers appears in the 1260-1180 cm^{-1} range.

-The C-H out of plane deformation for para-substituted benzene derivatives usually appear at 830 cm^{-1}. There is a peak at 826 cm^{-1} that could be assigned to this vibration. The peak at 1031 cm^{-1} is (as seen in the aniline spectrum) due to C-N stretching. Also, the N-H wagging is displayed at 800-666 cm^{-1}. The N-H bending produces a very small band at 1608 cm^{-1}.[26,29]

Methanesulfonic acid. This compound was analyzed under "Aniline : Methanesulfonic acid". (See page 80).

Mix. (See Figure 80.) The mix between p-methoxyaniline and methanesulfonic acid produces the same peak at about 2600 cm^{-1} that is possibly due to NH_3^+ stretching. This peak, at 2637 cm^{-1}, is sharper and higher than in the interaction aniline : methanesulfonic acid. P-methoxy is a ring activating group and should make a very strong interaction. There is still a band at about 3339 cm^{-1}. It is produced by the N-H stretching from aniline, the O-H stretching from the acid and the O-H stretching from methanol in the solvent. Methanol is a very hard compound to subtract.

The peaks at 1627 and 1512 cm^{-1} are due to asymmetric and symmetric NH_3^+ bending. These two bands are more clear than in the interaction with aniline.[29]

The peaks related to C-H and C-C linkages have relatively the same frequencies seen previously.

Other peaks that are displayed in the spectrum are the following:

C-S stretching is a strong peak at 675 cm^{-1}. This peak also combines the C-C bend ring.

The broad band with peaks at 1221 cm^{-1} and 1147 cm^{-1} is a combination of bond vibrations:

S=O (strong) usually 1300-1350 and 1150-1100 cm^{-1}.

C-O (strong) usually 1300-1200 cm^{-1}.

Para-substituted benzene derivatives display a peak at about 830 cm^{-1} due to C-H out of plane deformation. The spectrum shows a peak at 816 cm^{-1} for that vibration.[26]

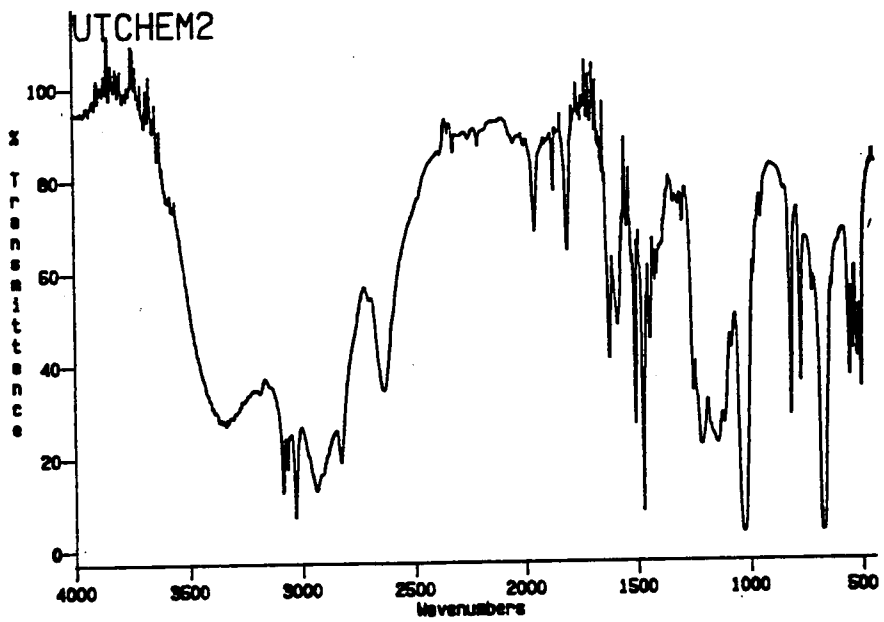


FIGURE 80. FTIR 80. p-Methoxyaniline : MSA mix. Mix after BM-75 subtraction (S.F.= 1.0). Ratio 1/1 in p-methoxyaniline : MSA interaction.

meta-Chloroaniline : Methanesulfonic acid. The 4N BM-75 solution of m-chloroaniline and the 0.8N BM-75 solution of methanesulfonic acid are both transparent. The mix (1 milliequivalent each) produces a snow white solid. The comparison between the last two interactions will give insight for understanding the ring activating (or deactivating) power of a group.

m-Chloroaniline. (See Figure 81.) It is an aromatic compound, very toxic and irritating. Its formula is $ClC_6H_4NH_2$. The spectrum analysis shows the following patterns:
The N-H stretching at about 3500-3300 cm^{-1} is uncommonly clear. Therefore, the subtraction works better than with p-methoxyaniline. The cause is probably due to an interaction with methanol (in solvent), which is weaker amid m-chloroaniline and methanol. The halogen deactivates the ring. The nitrogen electrons are pulled to the ring making the interaction with the solvent very weak.
The C-H aromatic stretching is displayed at 3086, 3066, and 3030 cm^{-1}, and normal C-H (due to solvent) is displayed in the 3000-2800 cm^{-1} zone.[26,29]
At 1611 cm^{-1}, N-H bending is very strong and at 1601 and 1481 cm^{-1} (sharp and strong peaks), C-C stretching appears. The peak at 1035 cm^{-1} is caused by the C-N stretching in primary amines. The strong peak at 676 cm^{-1} is due to C-C bend ring of benzene. Three small peaks appear between

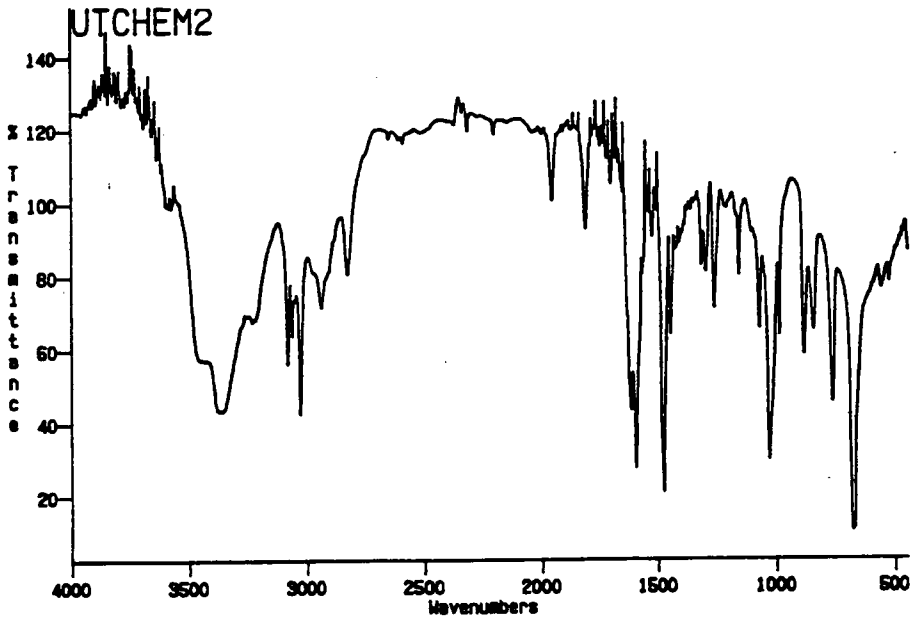


FIGURE 81. FTIR 81. Subtracted m-chloroaniline. m-Chloroaniline spectrum after BM-75 subtraction (S.F.= 0.7). Ratio 1/0 in m-chloroaniline : MSA interaction.

the two last peaks:

One, the peak at 885 cm^{-1}, could be produced by C-Cl anti-symmetric stretching. The two peaks at 848 and 764 cm^{-1} correspond to the m-substituted benzene derivatives. They display two bands that are caused by C-H out of plane deformation.[26]

Methanesulfonic acid. This compound was analyzed under "Aniline : methanesulfonic acid". (See page 80).

Mix. (See Figure 82.) M-Chloroaniline and methanesulfonic acid generate a spectrum that looks like the p-methoxyaniline : methanesulfonic acid spectrum. There is a new peak that does not appear in the single compound spectra. It has the same wavenumber, 2637 cm^{-1}, and the absorption is quite strong in both cases. Therefore, it is not possible to distinguish which one of the two groups (p-methoxy or m-chloro) is causing the strongest interaction.

Other peaks in the mix spectrum are the following:

-The band at 3351 cm^{-1} comes from the N-H stretching and the O-H stretching from acid and methanol.

-The C-H stretching, in the same region 3100-2800 cm^{-1}, includes aromatic and aliphatic vibrations.[26,29]

-The N-H bending, seen in the single compound, does not appear in this spectrum. Instead, there is a band which includes a peak at 1576 cm^{-1}. This peak is presumably due

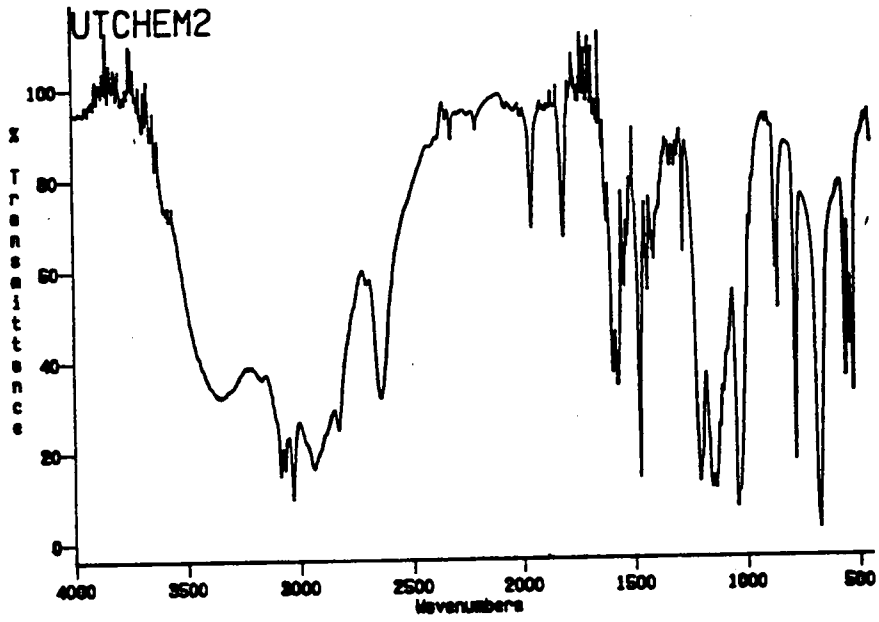


FIGURE 82. FTIR 82. m-Chloroaniline : MSA mix. Mix after BM-75 subtraction (S.F.= 0.7). Ratio 1/1 in m-chloroaniline : MSA interaction.

to the NH_3^+ symmetric bending.[29]

-The O-H bending (at about 1320 cm^{-1} in the acid spectrum) is not displayed in this spectrum. The S=O stretching vibration is in the mix spectrum at a lower frequency than in the acid spectrum.

-There are only two peaks among the C-N stretch (1034 cm^{-1}) and the C-C bend ring of benzene (679 cm^{-1}) while there were three in m-chloroaniline spectrum. The C-Cl stretching vibration appears lowered at 863 cm^{-1}. The C-H out of plane vibration for m-substituted benzene derivatives causes two bands (848 and 764 cm^{-1} in Figure 81). There is one peak at 784 cm^{-1}, which could be the peak at 764 cm^{-1} whose frequency was increased. The second peak could be included with the peak due to C-Cl stretching.

-The peaks at 1593, 1481, and 1439 cm^{-1} are produced by the C-C stretching in the ring. The peaks at 1956 and 1819 cm^{-1} are overtone bands for aromatic compounds.[26,29]

para-Methoxyaniline : Phenyl phosphinic acid. This interaction was studied to search for differences between the methoxy group and the halogen. Since phenyl phosphinic acid is weaker than methanesulfonic acid, it might be possible to distinguish the substituent effect on the interaction if the experiment is done with phenyl phosphinic acid.

The 1N BM-75 solution of p-methoxyaniline is brown and the

dilution in BM-75 (1 meq. p-methoxyaniline / 0 meq. PPA) is yellow. The 0.8N BM-75 solution of phenyl phosphinic acid is transparent as well as the dilution in BM-75 (0 meq. p-methoxyaniline / 1 meq. PPA).
When the two dilutions are placed together (1 meq. each), no solid is formed. However, there is visible change since the mix is darker than p-methoxyaniline dilution or 1/0.

p-Methoxyaniline. See p-methoxyaniline : methanesulfonic acid interaction (page 115) and Figure 79. The 1/0 dilution in this interaction gives the same peaks as in Figure 79.

Phenyl phosphinic acid. See Aniline : Phenyl phosphinic acid interaction (page 93) and Figure 68. There is reproducibility in the spectrum obtained in this investigation (BM-75 dilution with 0 meq. p-methoxyaniline/ 1 meq. phenyl phosphinic acid) with the phenyl phosphinic acid spectrum analyzed in that interaction.

Mix. (See Figure 83.) The mixture among p-methoxyaniline and phenyl phosphinic acid displays absorption bands in the 2800-2000 cm^{-1} region. These bands are new with regard to each compound alone. Hydrogen bonding lowers the stretching and raises the bending vibration frequencies.
The mix spectrum presents the following characteristics:
-The band due to O-H stretching was shifted and appears at

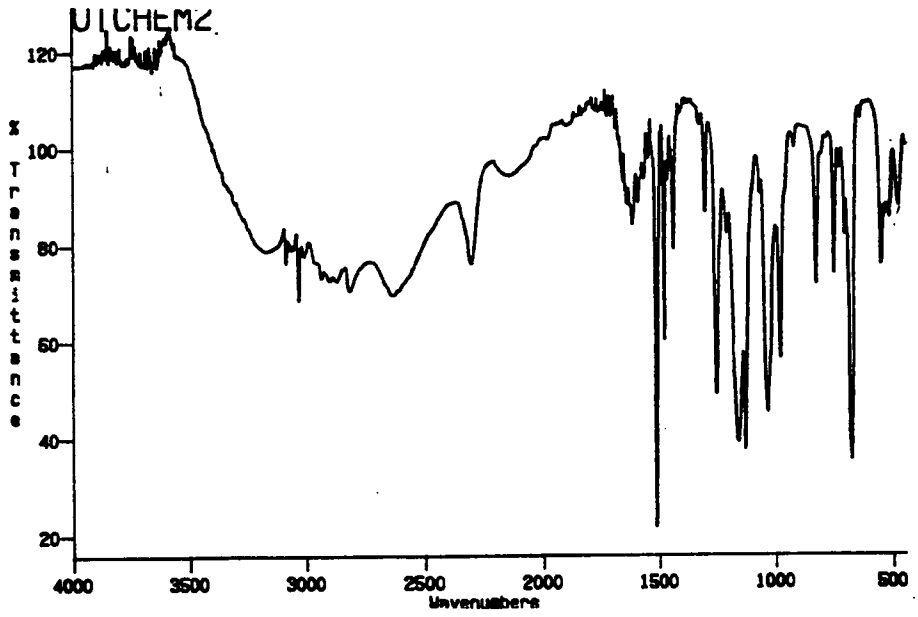


FIGURE 83. FTIR 83. p-Methoxyaniline : PPA mix. Mix after BM-75 subtraction (S.F.= 0.7). Ratio 1/1 in p-methoxyaniline : PPA interaction.

3190 cm^{-1}. The N-H stretching (same frequency) was also shifted.

-The C-H aromatic and C-H aliphatic stretching are displayed amid 3100 and 2800 cm^{-1}.[26,29]

-The P-H stretching appears lowered at 2310 cm^{-1}. The band at 2624 cm^{-1} (stronger absorption than P-H stretching) is probably due to interaction and hydrogen bond formation. A band that has the same cause is seen at 2126 cm^{-1}.

-The N-H bending has a strangely shaped band at 1612 cm^{-1}, and has a higher frequency than in the single compound.

-The C-C stretching in the ring appears lowered at 1510, 1480, 1437 cm^{-1}. The C-C bending appears at 676 cm^{-1}.

-The peak at 1250 cm^{-1} could be due to O-H bending (usually at 1208 cm^{-1}) and also to C-O stretching.

-The P=O stretching (at about 1200 cm^{-1} in PPA spectrum) is exposed in a band at 1161 cm^{-1}. The C-N stretching and phenyl group-P stretching are displayed at 1033 cm^{-1}. There are small peaks that come from either p-methoxyaniline or phenyl phosphinic acid.[26,29]

meta-Chloroaniline : Phenyl phosphinic acid. This interaction concludes the substituent effect study on model compounds. All solutions are transparent including the mixture: 4N BM-75 solution of m-chloroaniline, 0.8N BM-75 solution of phenyl phosphinic acid, and the dilutions in BM-75 with 1/0, 1/1 and 0/1 ratios in milliequivalents of

each compound.

m-Chloroaniline. See m-chloroaniline : methanesulfonic acid interaction (page 120) and Figure 81. The same peaks are obtained with dilution 1/0 in this interaction.

Phenyl phosphinic acid. See Aniline : Phenyl phosphinic acid interaction (page 93) and Figure 68.

Mix. (See Figure 84.) The interaction among m-chloroaniline and phenyl phosphinic acid is weaker than the one shown between para-methoxyaniline and phenyl phosphinic acid. When the two mix spectra are compared, it is feasible to observe that the band at about 2600 cm^{-1} with m-chloroaniline is weaker than the band with p-methoxyaniline.
The mix spectrum has bands and peaks as follows:
The 3500-3200 cm^{-1} region includes N-H stretching from m-chloroaniline and O-H stretching from phenyl phosphinic acid.
The 3100-2800 cm^{-1} zone contains C-H aromatic stretching from the compounds in the study, and the C-H aliphatic stretching due to methanol (from BM-75).[26,29]
The bands at 2613 and 2128 cm^{-1} reflect the hydrogen bond formed when the compounds are placed at once. The band between them is due to P-H stretching and appears at 2333 cm^{-1}. The P-H stretching is lowered compared to the PPA

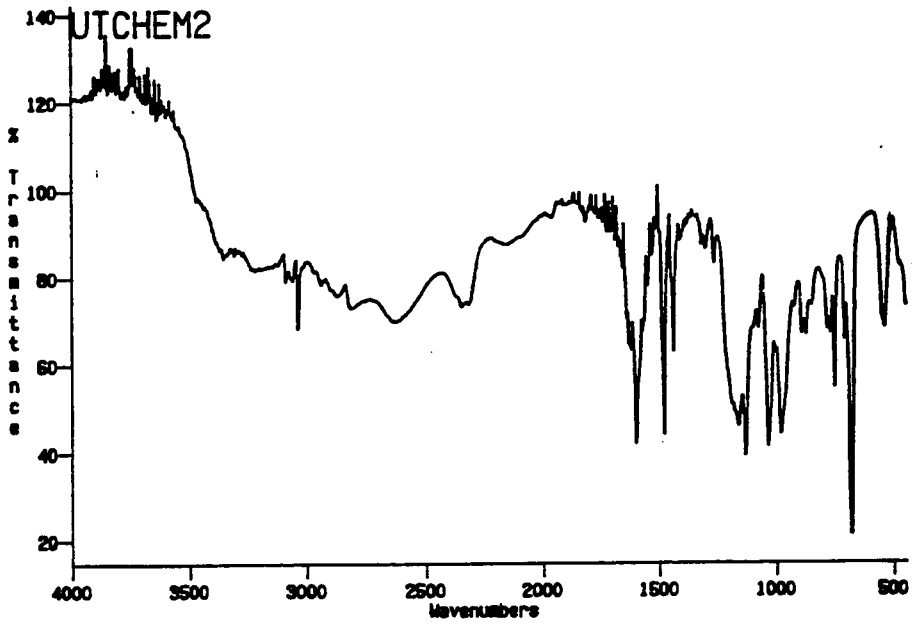


FIGURE 84. FTIR 84. m-Chloroaniline : PPA mix. Mix after BM-75 subtraction (S.F.= 0.6). Ratio 1/1 in m-chloroaniline : PPA interaction.

spectrum. The band at about 1600 cm^{-1} includes N-H bending. It is stronger than the band formed in the interaction with p-methoxyaniline (probably due to the weak bond).
P=O stretching is also lowered and appears at 1168 cm^{-1}. There is a peak in the band at about 1600 cm^{-1}. This peak and the peaks at 1482 and 1445 cm^{-1} are due to C-C stretching in the ring. They were not lowered with m-chloroaniline as they were with p-methoxyaniline.
After studying the substituent effect on model compounds, it is possible to notice differences with phenyl phosphinic acid. Methanesulfonic acid is such a strong acid that it makes differences difficult to recognize.

* Effect of Substituted Anilines on Polymer-Supported Reagents.

After investigating the substituent effect on model compounds, the study was done with polymeric sulfonic acid and polymeric phosphinic acid. The same substituted anilines were used in this research.

para-Methoxyaniline : Polymeric sulfonic acid. This interaction is carried out with a 1N BM-75 solution of p-methoxyaniline and the golden beads of polymeric sulfonic acid. The mixture with 1 meq. of each compound in BM-75 is left in contact for a 17-hour period. After the reaction, there is a change of color. The golden color of the beads changes

to an even darker gold.

p-Methoxyaniline. See p-methoxyaniline : methanesulfonic interaction (page 115) and Figure 79.

Polymeric sulfonic acid. See aniline : polymeric sulfonic acid interaction (page 105) and Figure 75.

Mix. (See Figure 85.) The mix among p-methoxyaniline and polymeric sulfonic acid gives a distinct bead colors and spectrum differences as follows:

The band with center at 3437 cm^{-1} is less strong than the band in the resin spectrum (Figure 75). The band is due to N-H stretching and O-H stretching combined.

The peaks (with no resolution) between 3100 and 2800 cm^{-1} are caused by C-H aromatic stretching and C-H stretching from methylene groups in the polymer backbone (vinyl group).

There is a strong peak at 2611 cm^{-1} that is probably produced by the interaction. Between 1660 and 1610 cm^{-1}, NH_3^+ has an asymmetric bending, and in the 1550-1485 cm^{-1} region, it has a symmetric bending (strong). The C-C stretching in the ring also displays peaks in this region.[26,29]

The band in the 550-500 cm^{-1} range also changes. This could be due to the torsional oscillation of the NH_3^+ group which is close to 500 cm^{-1}.

Other peaks and bands come from either one compound or the

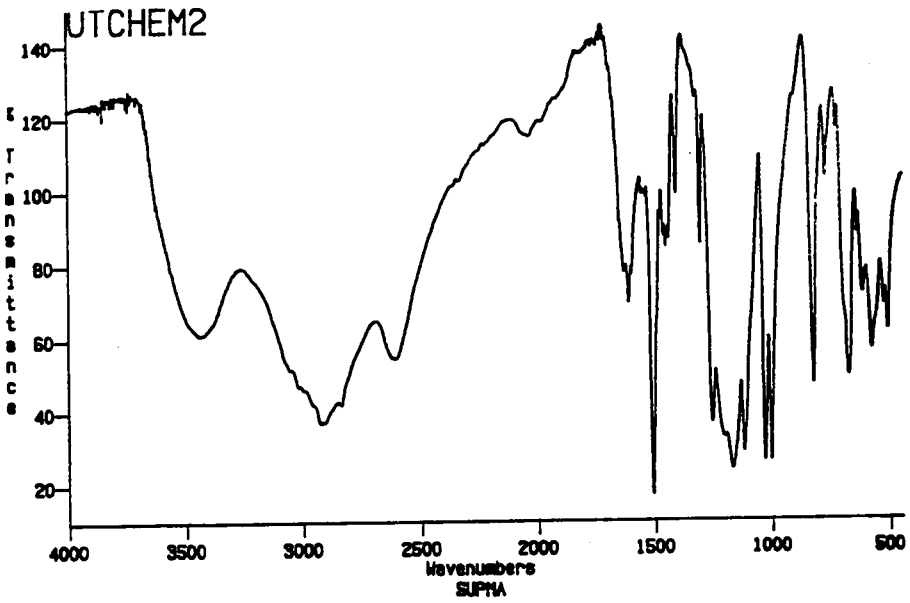


FIGURE 85. FTIR 85. p-Methoxyaniline : polymeric sulfonic acid mix. Spectrum recorded with a KBr pellet.

other. For example, the very broad band between 1258 and 1123 cm^{-1} is a combination of S=O stretching from the polymer, C-O-C stretching from aryl alquil ethers and C-H in plane bending.

The C-H out of plane deformation in para-substituted benzene derivatives (832 cm^{-1} for the polymer and 822 cm^{-1} for p-methoxyaniline) appears to be very strong in the mix. The wavenumber is 825 cm^{-1}.

The peaks at about 1000 and 1030 cm^{-1} are due to C-H stretching and out of plane C-H bending. At 678 cm^{-1}, C-C stretching appears.[26,29]

meta-Chloroaniline : Polymeric sulfonic acid. When these two compounds (1 meq. each in BM-75 solution) are placed together for a 17-hour period, there is a visible modification. The 4N BM-75 solution of m-chloroaniline is transparent. The polymeric sulfonic acid beads are golden. The resulting beads are very light golden.

m-Chloroaniline. See m-chloroaniline : methanesulfonic acid interaction (page 120) and Figure 81.

Polymeric sulfonic acid. See aniline : polymeric sulfonic acid interaction (page 105) and Figure 75.

Mix. (See Figure 86.) The mix spectrum produced by the m-chloroaniline : polymeric sulfonic resin interaction shows the same bands with the same infrared absorption as the last interaction. It seems that the substituent group does not make any difference to the strength of the interaction. Some of the differences are due to C-Cl stretching, which appears at 869 cm^{-1}, or the two bands due to the meta-substituted benzene derivatives.[26]

para-Methoxyaniline : Polymeric phosphinic acid. As in the two last interactions, this combination produces a color difference. The polymeric phosphinic acid beads have a snow white color. The 1N BM-75 solution of p-methoxyaniline has a brown color. The mix has 1 milliequivalent of each compound. After a 17-hour contact period, the mix beads have a dark tan color. The spectrum was recorded with a KBr-pellet after drying the solvent.

p-Methoxyaniline. See p-methoxyaniline : methanesulfonic acid interaction (page 115) and Figure 79.

Polymeric phosphinic acid. See aniline : polymeric phosphinic acid interaction (page 110) and Figure 77.

Mix. (See Figure 87.) The mixture between p-methoxyaniline and polymeric phosphinic acid displays the following

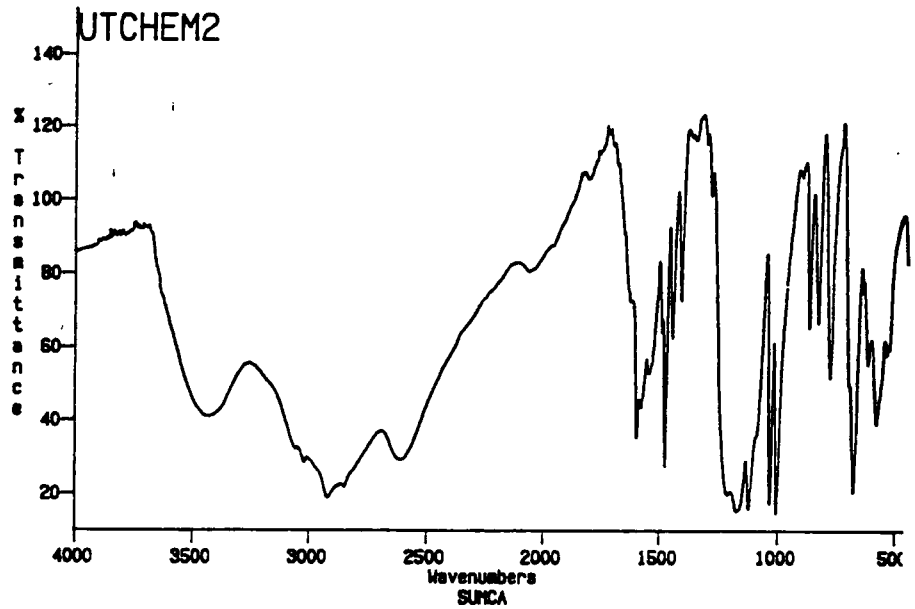


FIGURE 86. FTIR 86. m-Chloroaniline : polymeric sulfonic acid mix. Spectrum recorded with a KBr pellet.

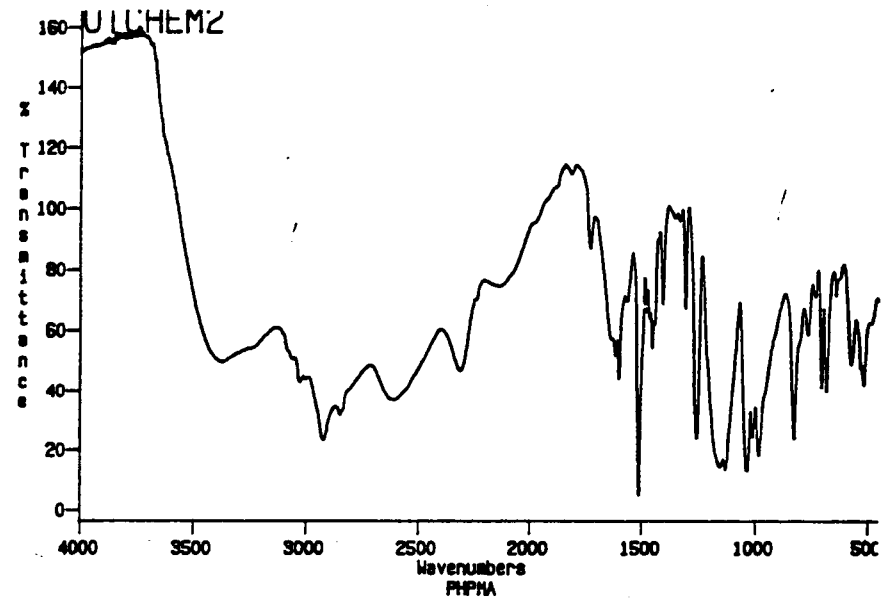


FIGURE 87. FTIR 87. p-Methoxyaniline : polymeric phosphinic acid mix. Spectrum recorded with a KBr pellet.

bands and peaks in its spectrum:

The band at 3367 cm^{-1} is due to N-H stretching and O-H intermolecular bonding.

The C-H aromatic stretching was lowered and appears at 3087, 3062, and 3020 cm^{-1}. The C-H stretching from methylene groups in the polymer backbone is displayed at 2918 and 2846 cm^{-1} (lower frequency than single compound).[26,29]

The band at 2597 cm^{-1} is caused by the interaction of the compounds. There is a hydrogen bond formation.

The region below 2000 cm^{-1} is really hard to characterize because of the overlap of bands. These compounds are two benzene derivatives, and one of them is a polymer chain. Some of the stretching frequencies are lowered and the bending frequencies are raised. This is produced by hydrogen bonding.

meta-Chloroaniline : Polymeric phosphinic acid. This was the last interaction studied. As told before, the mixture produces color differences. The 4N BM-75 solution of m-chloroaniline is transparent. Polymeric phosphinic acid beads are snow white. The mix beads are very light tan.

m-Chloroaniline. See m-chloroaniline : methanesulfonic acid interaction (page 120) and Figure 81.

Polymeric phosphinic acid. See aniline : polymeric phos-

phinic acid interaction (page 110) and Figure 77.

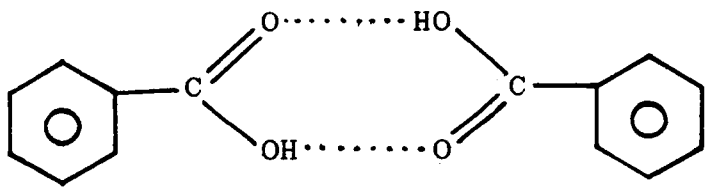
Mix. (See Figure 88.) The mix among m-chloroaniline and polymeric phosphinic acid gives a smaller peak at 2600 cm^{-1} than is shown with p-methoxyaniline. It is easy to determine if the P-H stretching (right side, at 2344 cm^{-1}) is the reference.

The other peaks are already studied in former interactions. The most important difference in this spectrum is that peak which is caused by hydrogen bond formation.

* Strength of Intermolecular Hydrogen Bond.

(Solid vs. Solution)

Benzoic acid. The benzoic acid (solid) spectrum (Figure 89) displays several bands between 3000 and 2500 cm^{-1}. These bands are connected with an acid that forms a hydrogen bond. Benzoic acid is a dimer as shown:



The C-H aromatic stretching appears at 3100-3000 cm^{-1} in this spectrum. The C=O stretching is the strong band at 1692 cm^{-1}. All the peaks below 1600 cm^{-1} are related to the aromatic frequencies belonging to the benzene ring.[26,29]

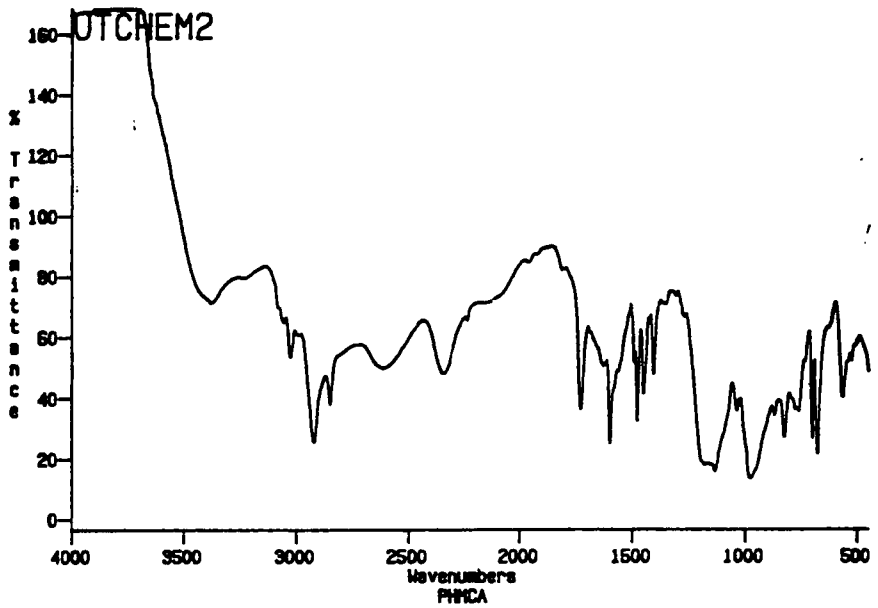


FIGURE 88. FTIR 88. m-Chloroaniline : polymeric phosphinic acid mix. Spectrum recorded with a KBr pellet.

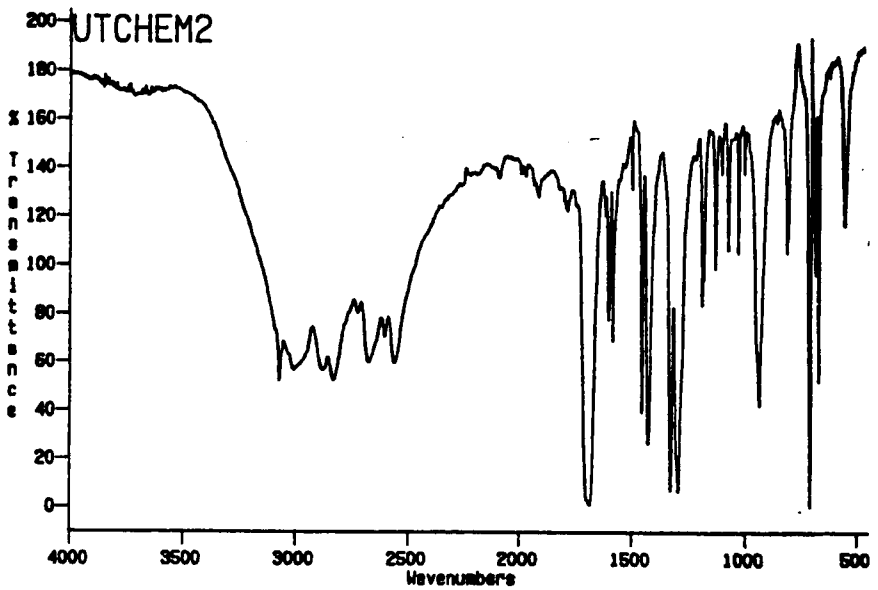


FIGURE 89. FTIR 89. Solid benzoic acid. (KBr pellet.)

Benzoic acid in BM-75 has a different spectrum due to environmental changes (Figure 90). The bands are combined. There are bands and peaks from benzoic acid, benzene, and methanol.

The spectrum displays the following bands or peaks:

-Free O-H (no resolution) at 3595 cm^{-1}.

-Intermolecular O-H bonded at 3335 cm^{-1}.

-Aromatic C-H stretching at 3100-3000 cm^{-1}.

-Methyl C-H stretching at 3000-2800 cm^{-1}.

-Weak bands for hydrogen bond at 2622, 2516 cm^{-1}.

-Overtone bands for aromatic compounds at 1954, 1815 cm^{-1}.

-Stretching of carbonyl (C=O) group at 1699 cm^{-1}.

-Stretching of C-C at 1483 cm^{-1}.

-Bending of O-H at 1396 cm^{-1}.

-Stretching of C-O at 1265 cm^{-1}.

-Out of plane C-H bending at 1027 cm^{-1}.

-C-C bending in the ring for both benzene and benzoic acid at 675 cm^{-1}.[26,29]

After the benzoic acid in solution was analyzed, the subtraction technique was applied. The procedure was done twice, trying to remove the solvent (BM-75) completely. This spectrum is shown in Figure 91. There is still a small band due to methanol. The peaks between 3000 and 2500 cm^{-1} try to appear as solid benzoic acid peaks. The region below 1600 cm^{-1} is particular to aromatic compounds.

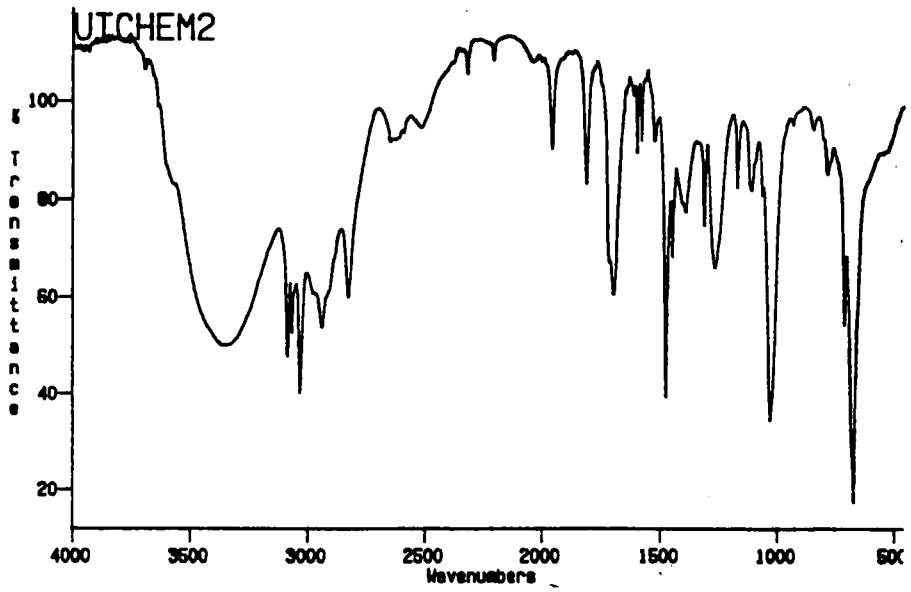


FIGURE 90. FTIR 90. Benzoic acid in BM-75.

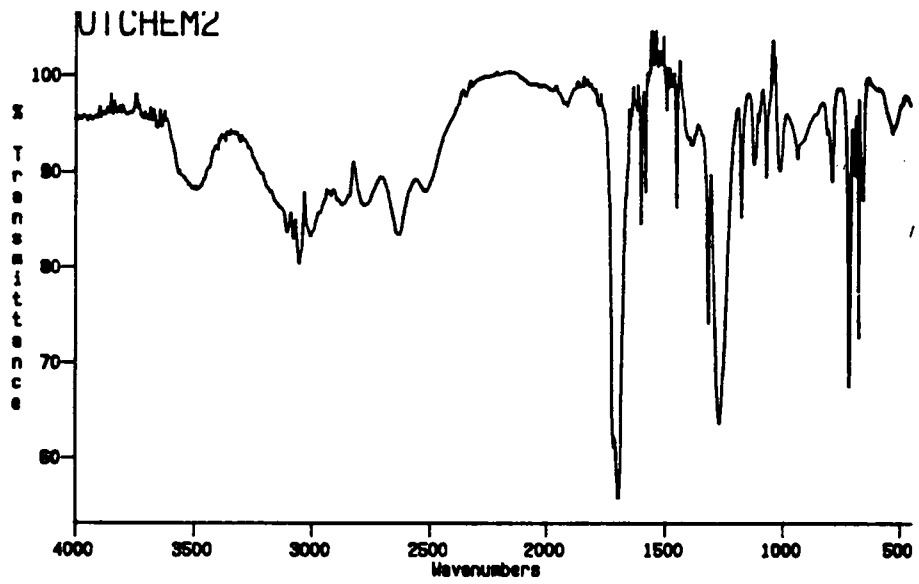
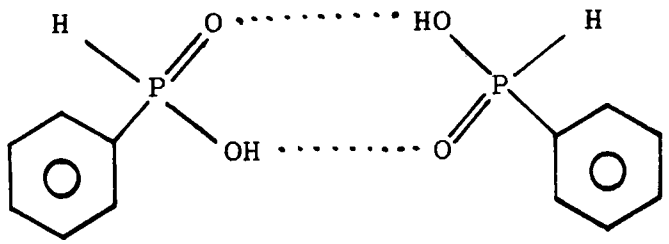


FIGURE 91. FTIR 91. Subtracted benzoic acid. Benzoic acid spectrum after BM-75 subtraction. (1) S.F.= 0.6 (2) S.F.= 0.15.

Phenyl phosphinic acid. The spectrum of the solid compound was recorded and is shown in Figure 92. There is a greater shift in the bands due to hydrogen bond than with benzoic acid. The bands are displayed between 3000 and 2000 cm^{-1}. The phenyl phosphinic acid configuration as solid is shown:



The region below 1700 cm^{-1} is hard to interpret because of aromatic frequencies and P=O and P-OH frequencies. P-H stretching is displayed at about 2300 cm^{-1}.[29]

When the phenyl phosphinic acid is dissolved in BM-75 (see Figure 93) the bands are from the three compounds as in the benzoic acid study.

The subtraction of the solvent from the BM-75 solution of phenyl phosphinic acid is shown in Figure 94. Methanol is really an arduous compound to subtract by FTIR analysis.

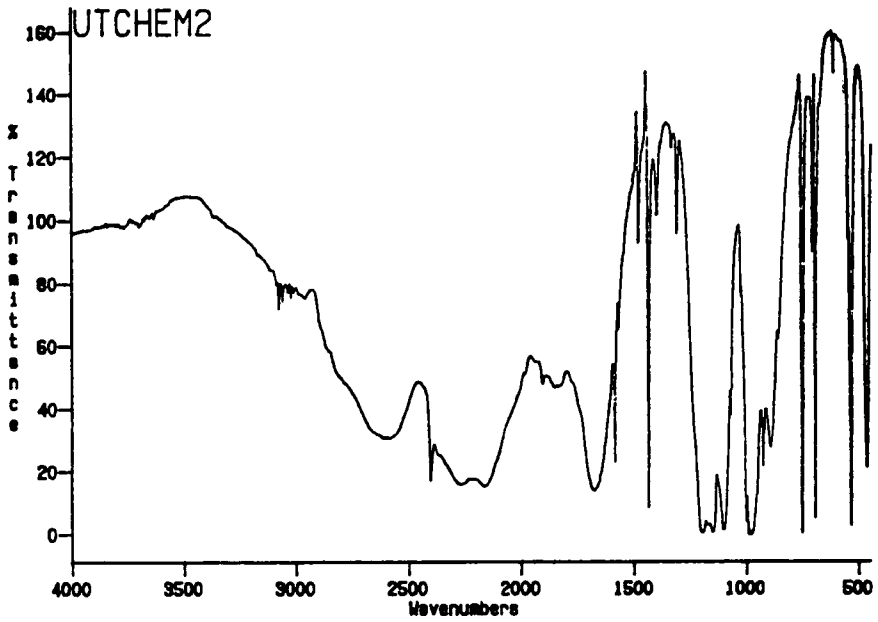


FIGURE 92. FTIR 92. Solid phenyl phosphinic acid. (KBr pellet.)

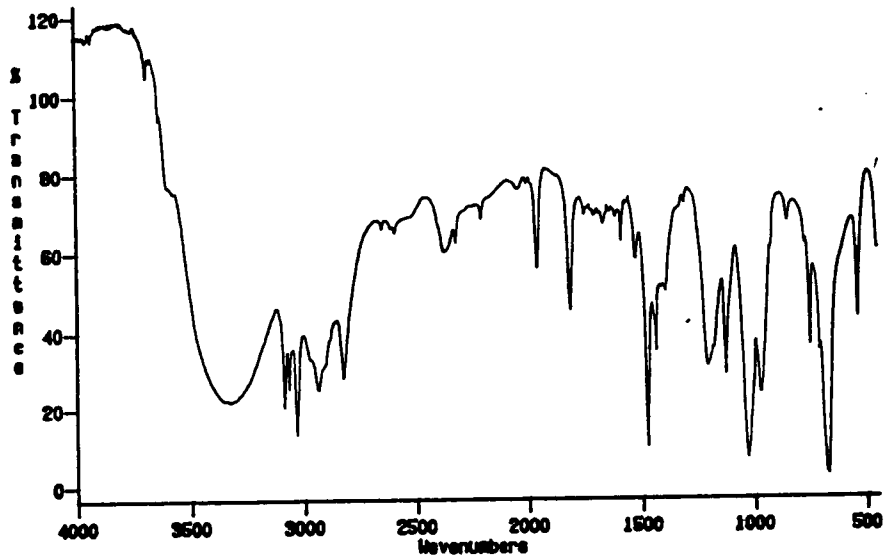


FIGURE 93. FTIR 93. Phenyl phosphinic acid in BM-75.

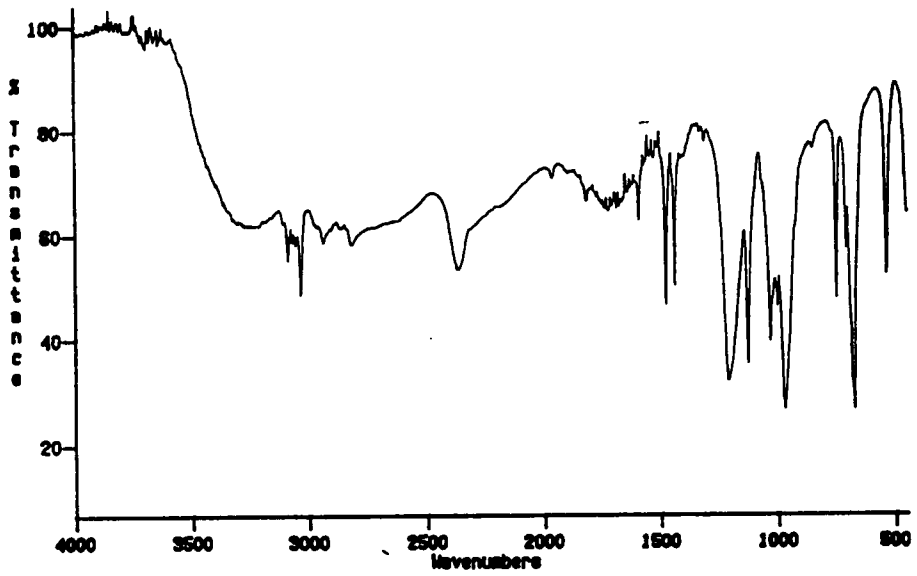


FIGURE 94. FTIR 94. Subtracted phenyl phosphinic acid. Phenyl phosphinic acid spectrum after BM-75 subtraction.

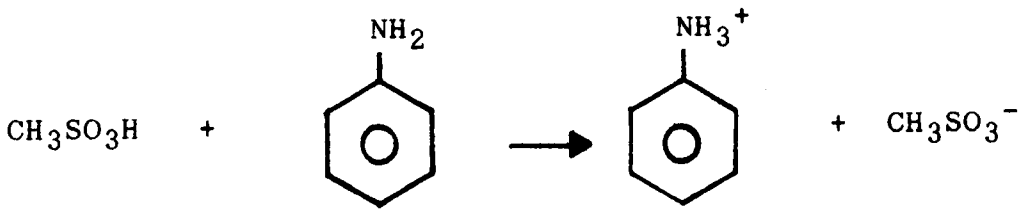
CHAPTER V

CONCLUSIONS

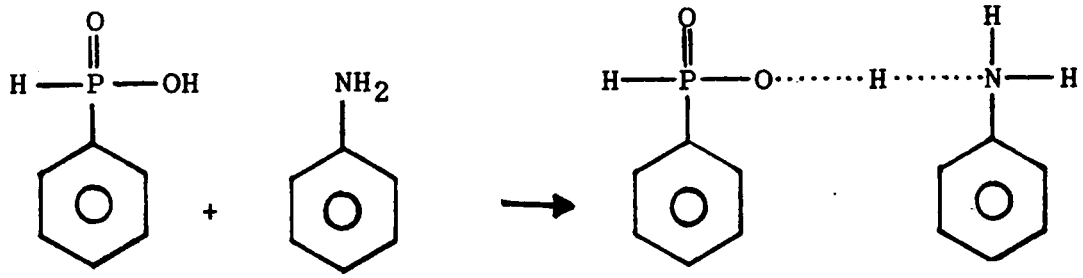
The current investigation gives an understanding about how polymeric sulfonic acid and polymeric phosphinic acid interact with molecules. Polymer-supported reagents react with the compounds selected depending on their acidity. The FTIR analysis performed through model compounds studies shows:

MODEL COMPOUNDS.

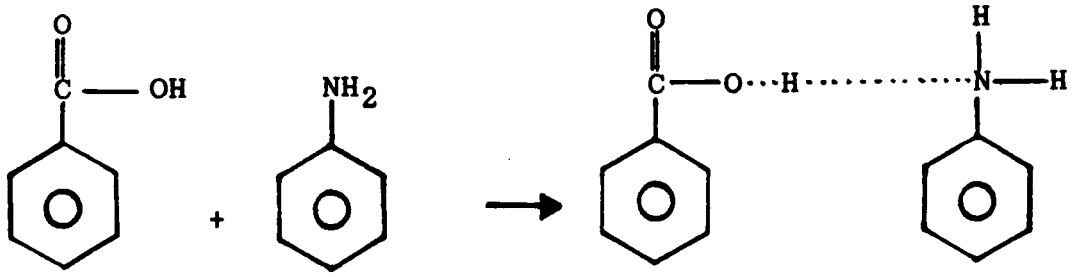
1. The study shows that methanesulfonic acid and aniline interact strongly. The formation of a salt, the anilinium ion, due to a proton transfer from the acid to aniline (a base) is observed as a new strong peak at about 2600 cm^{-1} in the mix spectrum. The complete reaction takes place at a ratio of one milliequivalent of aniline : one milliequivalent of methanesulfonic acid.



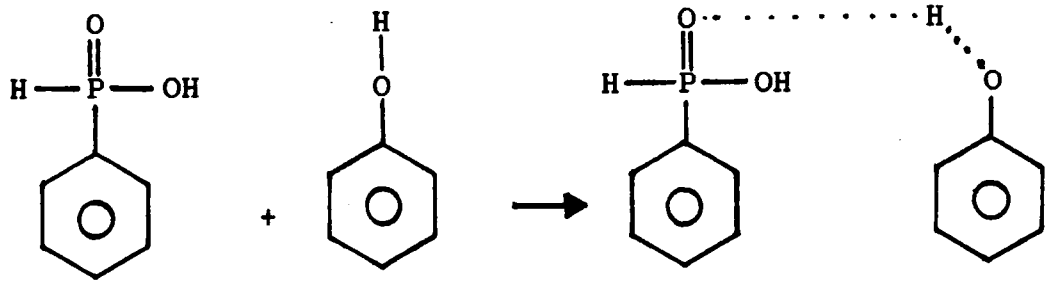
2. Phenyl phosphinic acid and aniline have a weaker interaction between them. The product is the formation of a hydrogen bond. There is no solid formation, but the stretching frequencies are lowered in the mix spectrum. Besides, the bending vibrations have higher frequencies in the mix spectrum than in the single compound. There is a new broad band at about 2600 cm^{-1} in the mix. The complete reaction takes place when there is also one milliequivalent of each compound.



3. Benzoic acid and aniline (1 meq. each) interact forming a weaker hydrogen bond than the one between aniline and phenyl phosphinic acid. There are small differences in the mix spectrum.

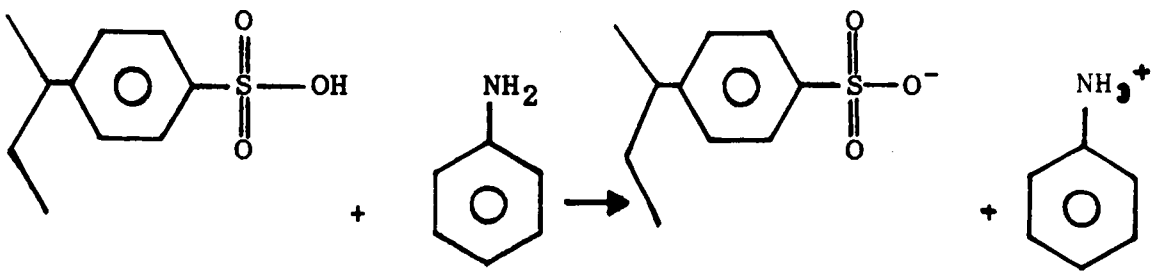


4. Phenyl phosphinic acid and phenol also interact weakly.

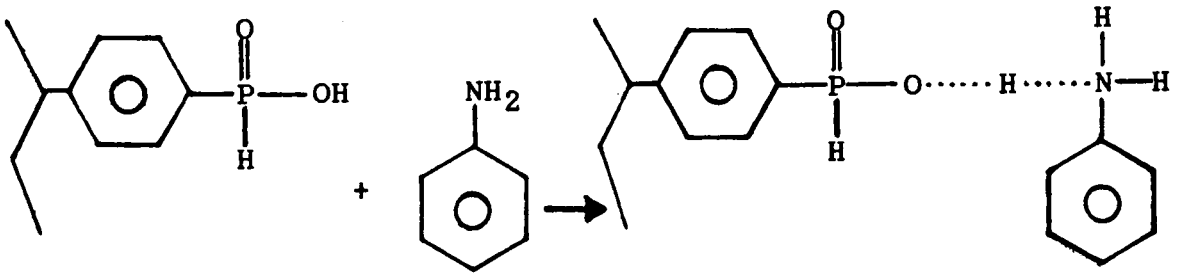


POLYMER COMPOUNDS.

1. Polymeric sulfonic acid and aniline (1 meq. each) interact by proton transfer, with formation of anilinium ion after a 17-hour contact reaction. The color of the resin beads changes after reaction and a strong band is evident at about 2600 cm^{-1} in the mix spectrum.



2. Polymeric phosphinic acid and aniline (1 meq. each) interact with the formation of hydrogen bond after a 17-hour contact reaction. The color of the resin beads also changes and some characteristics of the hydrogen bond are displayed in the mix spectrum.



SUBSTITUENT EFFECT.

For model compounds, p-methoxyaniline and m-chloroaniline react with methanesulfonic acid producing small differences in the new peak at about 2600 cm^{-1}. The absorption is almost identical. Therefore, it is very difficult to characterize the reaction regarding the substituent group of the benzene ring. Methoxy is an electron donor which activates the ring. On the contrary, a halogen is an electron withdrawer which deactivates the ring.

Regarding phenyl phosphinic acid, p-methoxyaniline reacts with this compound producing a stronger absorption

at about 2600 cm^{-1} than with m-chloroaniline. The P-H stretching frequency at 2300 cm^{-1} is the absorption band reference. Phenyl phosphinic acid yields specificity related to substituent effect.

Regarding polymer-supported reagents, the interaction among polymeric sulfonic acid and aniline derivatives is very strong. The band at about 2600 cm^{-1} is similar in both cases, with p-methoxyaniline and with m-chloroaniline. This does not allow us to differentiate clearly between the activating power and the deactivating power of a particular group to a benzene ring.

Polymeric phosphinic acid gives a better understanding of the substituent effect. The interaction between p-methoxyaniline and this resin yields a stronger absorption band than the obtained band between m-chloroaniline and this polymer-supported reagent. Polymeric phosphinic acid provides a better selectivity.

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APPENDICES

APPENDIX A

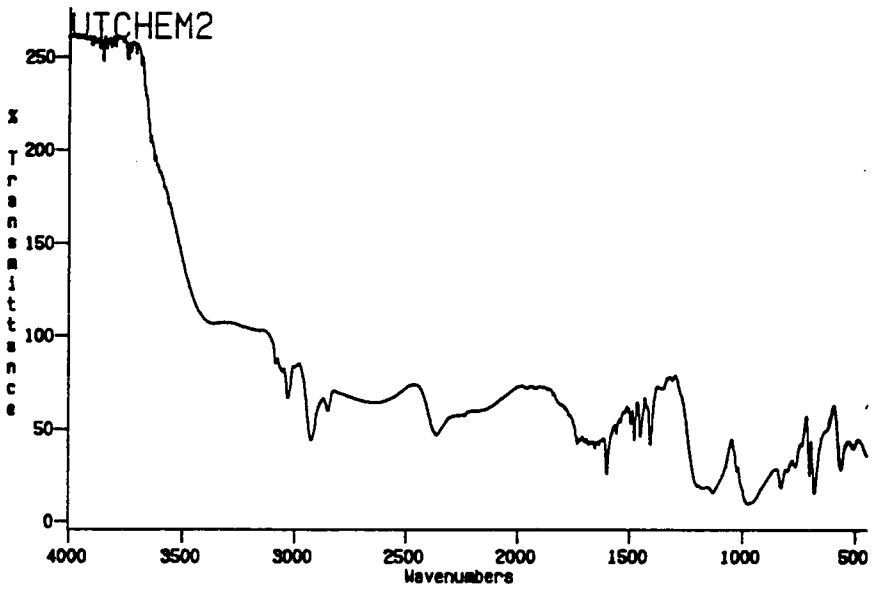
POLYMERIC PHOSPHINIC ACID (KBr PELLET)

This analysis is carried out with the polymeric phosphinic acid beads in order to find the best concentration of the sample in the KBr pellet, and at the same time, to get the best spectrum for this research.

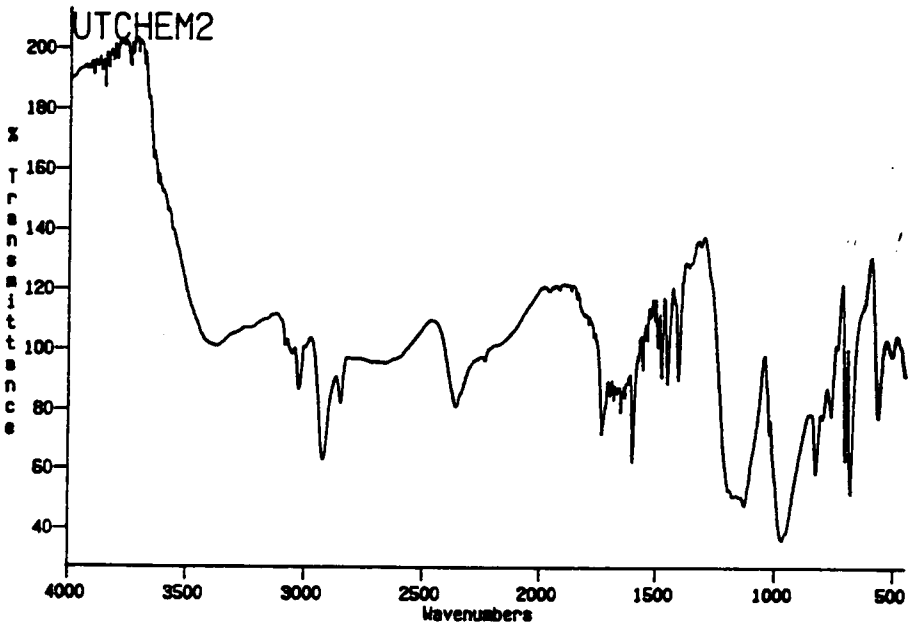
The first spectrum is found with a KBr pellet of 0.150 g , that is, 3% of sample and 97% of KBr (IR powder) (see Figure 95 - FTIR 95). The powder is ground for about 3-5 minutes and then pressed for 6-8 minutes. The KBr cell is placed in one direction for 1 minute (8,000 lb/in^2), and in the opposite direction for about 6-8 minutes (16,000 lb/in^2). This was performed with all the samples.

The second spectrum is accomplished with a KBr pellet of 0.130 g and a bead sample of 3%. This spectrum is shown in Figure 95 (FTIR 96). Another determination is practiced with 2.5% of sample in a KBr pellet of 0.130 g (see Figure 95 - FTIR 97).

The fourth test is carried out with 3% of sample in a KBr pellet of 0.120 g (see Figure 95 - FTIR 98). Finally, the best spectrum is obtained with a KBr pellet of 0.120 g having 2.5% of sample. This spectrum is used in the Aniline : Polymeric phosphinic acid interaction in Chapter III (see page 110).

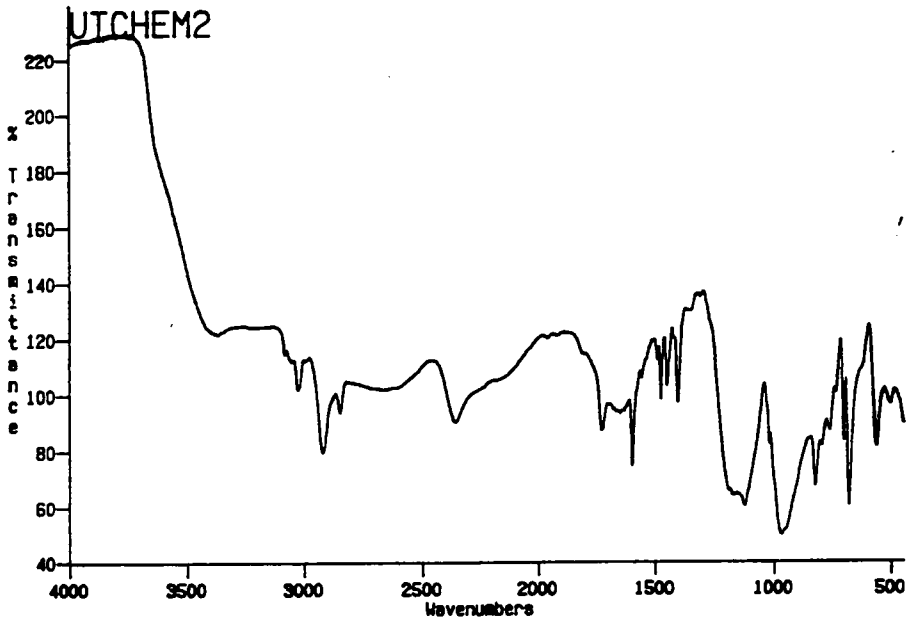


FTIR 95. Polymeric phosphinic acid. KBr pellet of 0.150 g with 3% of sample.

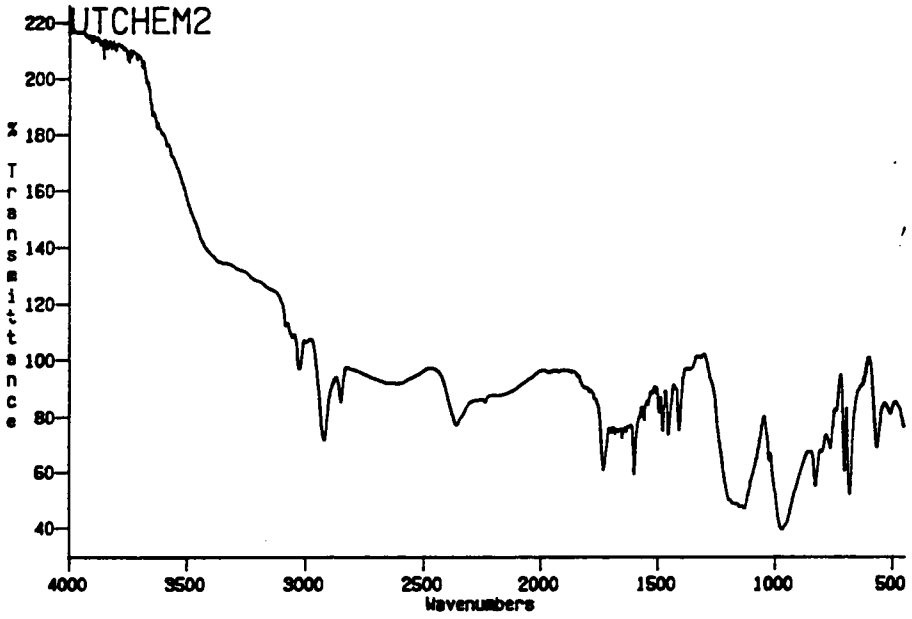


FTIR 96. Polymeric phosphinic acid. KBr pellet of 0.130 g with 3% of sample.

FIGURE 95. FTIR 95-98.



FTIR 97. Polymeric phosphinic acid. KBr pellet of 0.130 g with 2.5% of sample.



FTIR 98. Polymeric phosphinic acid. KBr pellet of 0.120 g with 3% of sample.

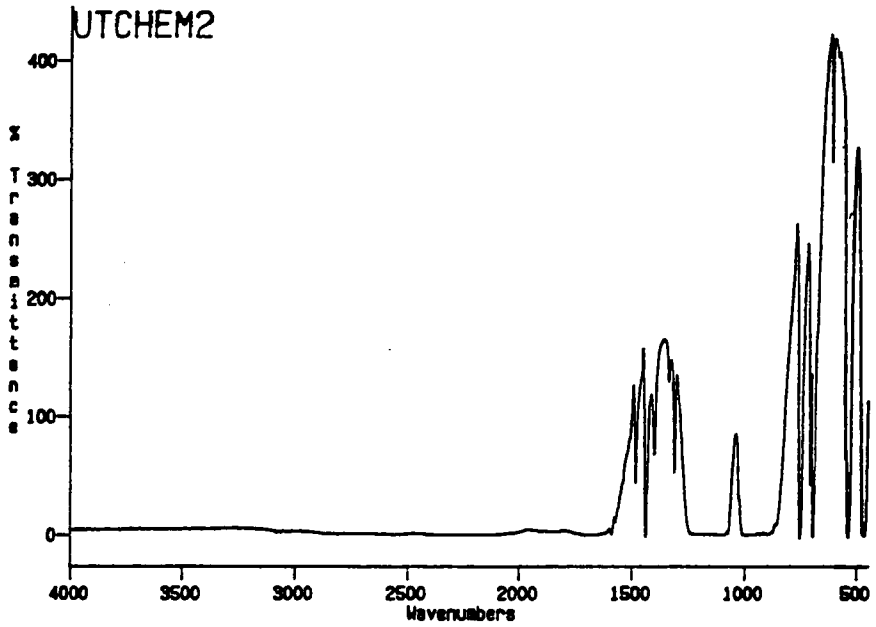
FIGURE 95. (Continued)

APPENDIX B

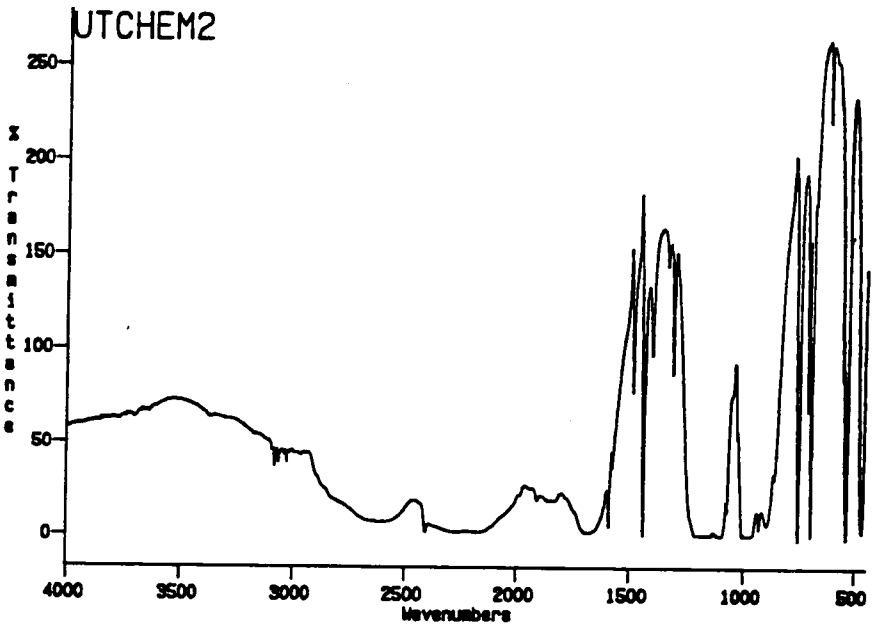
PHENYL PHOSPHINIC ACID (KBr PELLET)

This study is performed to obtain an acceptable spectrum for phenyl phosphinic acid (solid) and to compare it with its spectrum in BM-75 solution, and with its subtracted spectrum. Several tests are done with different weights of sample and KBr pellets. Once weighed, the powder is ground for about 3 minutes and pressed for 7 minutes (same conditions as in APPENDIX A). The following tests are carried out:

1) The weight of the pellet is 0.130 g and the sample is 3% of the pellet (Figure 96 - FTIR 99). There is no transmittance because the pellet thickness is bigger than the appropriate.
2) The weight of the pellet is 0.120 g and the sample is 2.5% of the pellet (Figure 96 - FTIR 100). This test produces an improved spectrum than the first test, but it is not acceptable.
3) The weight of the pellet is 0.120 g and the sample is 0.5% of the pellet (Figure 96 - FTIR 101). This percentage produces a much better spectrum for the analysis.
4) The weight of the pellet is 0.130 g and the sample is 0.6% of the pellet (Figure 96 - FTIR 102).

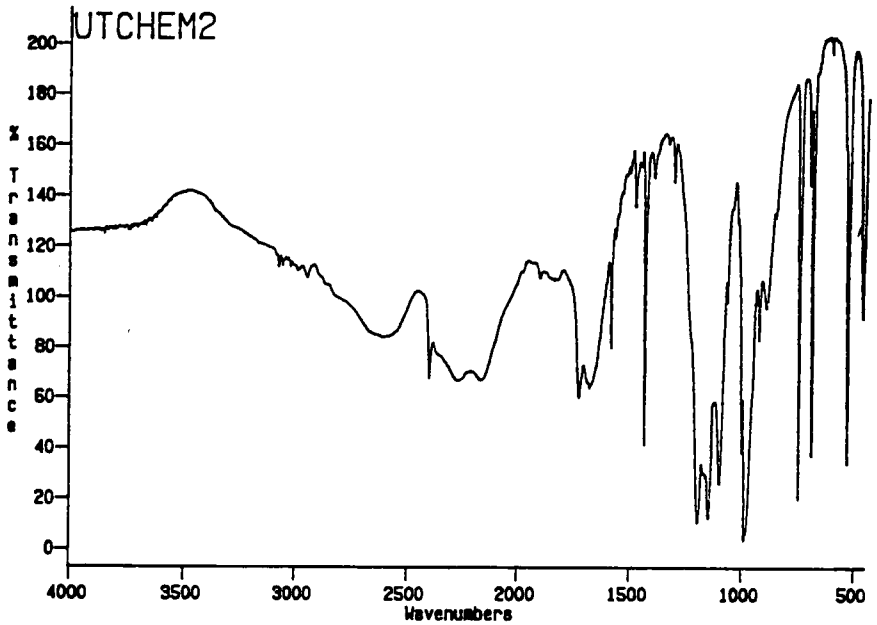


FTIR 99. Phenyl phosphinic acid. KBr pellet of 0.130 g with 3% of sample.

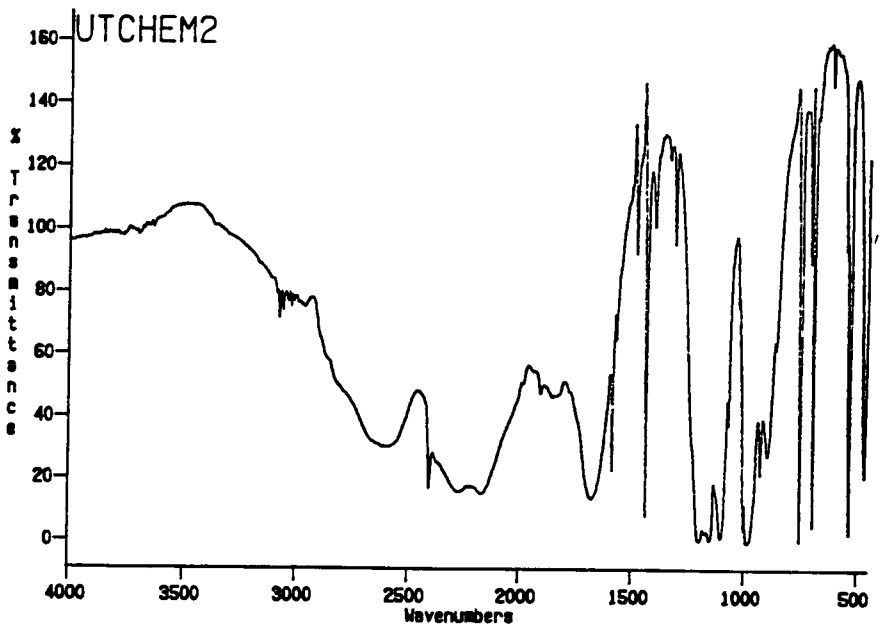


FTIR 100. Phenyl phosphinic acid. KBr pellet of 0.120 g with 2.5% of sample.

FIGURE 96. FTIR 99-102.



FTIR 101. Phenyl phosphinic acid. KBr pellet of 0.120 g with 0.5% of sample.



FTIR 102. Phenyl phosphinic acid. KBr pellet of 0.130 g with 0.6% of sample.

FIGURE 96. (Continued)

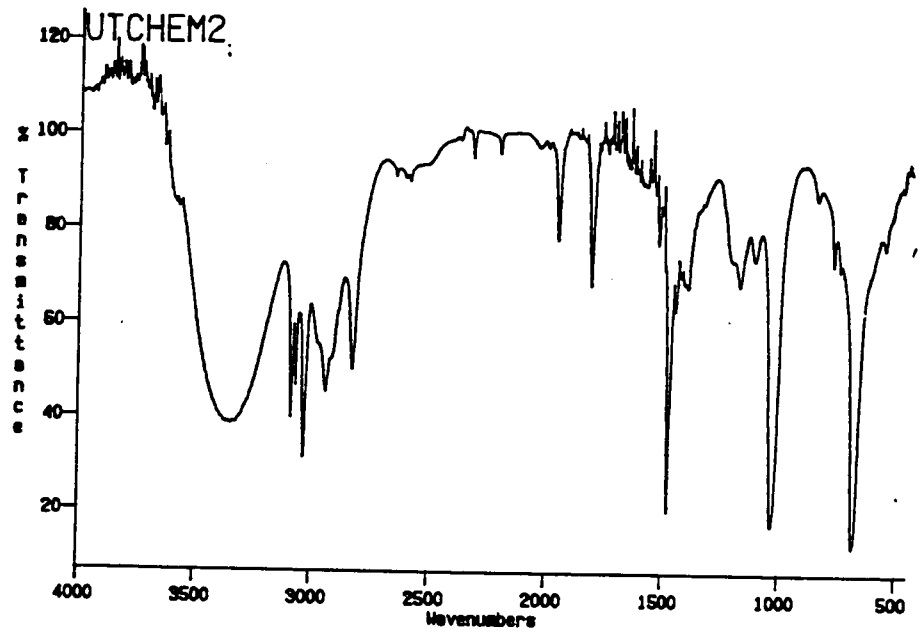
This is the last test. This also yields an acceptable spectrum. Analyzing all of the spectra, their transmittance and their peak resolution, the spectrum obtained in the third test (Figure 96 - FTIR 101) is considered the best.

APPENDIX C

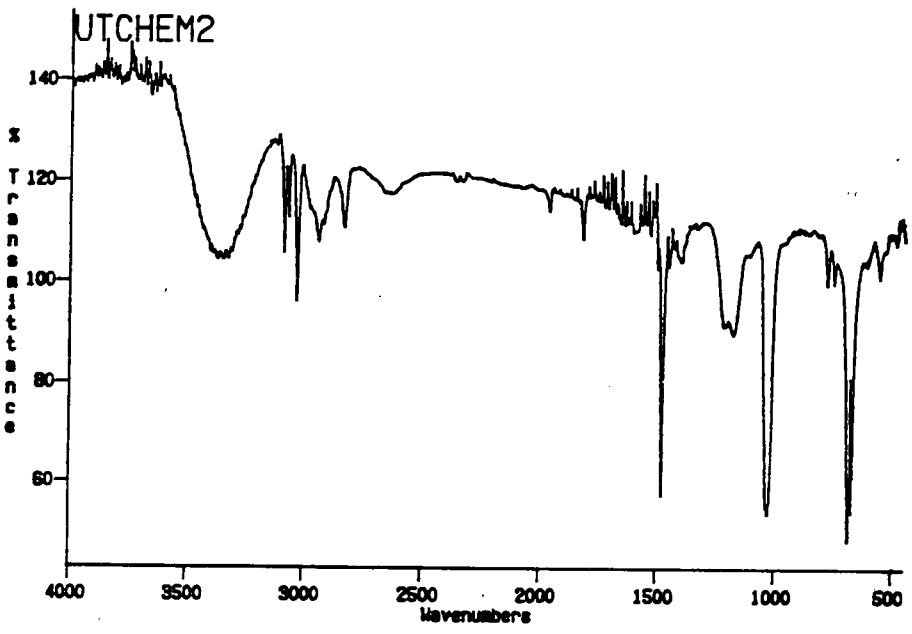
BENZENE-METHANOL SUBTRACTION

Solvent subtraction is an important operation in this research. Subtraction gives satisfactory results when the conditions are followed to perfection. When the spectrum of benzene-methanol (75/25), loaded into the FTIR computer memory, is subtracted from the same spectrum utilizing 0.5 as S.F., the result is the benzene-methanol spectrum. When the subtraction factor is increased to 1.0, the result is a perfect horizontal line in the middle of the screen. For that reason, no compound is present.

Recalling the aniline : methanesulfonic acid interaction, the subtracted spectrum of the liquid portion of the mix (5T-BM; S.F.=0.6) looks like benzene-methanol. In order to remove more solvent (and get a straight line), two more subtractions are done to this already subtracted spectrum. The factors are determined from the display field. For the first subtraction, 0.5 is used as the S.F. For the second subtraction, 1.4 is used as the factor. It is not possible to increase the S.F. further than 1.4. The first subtraction is shown in Figure 97 (FTIR 103) and looks like BM-75 mix. The second is shown in Figure 97 (FTIR 104). Although more solvent has been removed, BM-75 is still present.



FTIR 103. Subtracted BM-75. (S.F.= 0.5)



FTIR 104. Subtracted BM-75. (S.F.= 1.4)

FIGURE 97. FTIR 103-104.

VITA

Rosario Munoz-Martinez was born in Cartagena, a resort on the north coast of Colombia, South America. She attended a Catholic high school in her city where she received her diploma in November 1973. She attended The College of Chemistry and Pharmacy at The University of Cartagena, Colombia where her Bachelor's degree was awarded with honors in December 1980. For her Bachelor's degree, she presented a thesis entitled "Scientific and Economic Evaluation of Emulsifiers and Stabilizers in Ice Cream."

During 1978-1980, she worked for a detergent production company as a part-time employee, and from 1980 to 1986 as a part-time worker for a clinical laboratory. From August 1983 she began to work as a part-time teacher in The Department of Chemistry, at The University of Cartagena which gave her a full-time position in 1987. This allowed her to apply for the scholarship to study abroad. She came to UTK as a student in a exchange program of American and Latin American Universities in August 1988. She received the M.S. degree in August 1990.