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CONFORMATIONAL CHANGES IN POLYELECTROLYTES

AND THE EFFECT ON METAL BINDING

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ABSTRACT

There has been considerable interest in the complexation of metals and other cations by natural humic and fulvic acids, as well as synthetic polyelectrolytes. In order to explain the binding observed for metals, and other species by organic polyelectrolytes, steric effects have been proposed. In this work, the effects of pH changes in aqueous solution on two synthetic polyelectrolytes, polymaleic acid (PMA) and polyacrylic acid (PAA), have been examined by laser Raman spectroscopy and turbidity measurements. These results are compared to Fourier-transform infrared (FTIR) and (^{13}C) nuclear magnetic resonance (NMR) spectra for solid samples of PMA, PAA, and fulvic and humic acids. Two types of carboxylic acid groups were detected for PMA in aqueous solution. Crystallization of PMA in a narrow pH range was observed. These data are consistent with strong intramolecular hydrogen bonding occurring in PMA at a pH of approximately 4. This implications of these results on the use of these compounds as models for fulvic and humic acids is discussed

INTRODUCTION

Humic and fulvic acids (collectively termed "humics") are important naturally occurring complexing and redox agents for a variety of metals and other chemical species. Increasing concerns about groundwater quality and contamination of soils and waters by hazardous wastes has emphasized the need to understand the role of these polyelectrolytes in ecological processes. Because of the complex chemical and physical structure of the humics, a number of simpler synthetic polyelectrolytes have been proposed as model systems,[1-5] such as polyacrylic acid (PAA) and polymaleic acid (PMA). It is interesting that these synthetic polyelectrolytes have found applications ranging from medicinal chemistry to industrial applications, particularly in the areas of water purification and immunology.[6-10]

In order to adequately describe the complexation of metals by anionic polyelectrolytes, it has been found that conformational behavior must be incorporated into any useful modeling effort.[11-14] Observation of considerable variability between the potentiometric behavior of synthetic and of natural polyelectrolytes and differences in their apparent acid constants for different counter-ions has led to conflicting results between laboratories, and has led to proposals that polymer hetereogeneities, impurities, and inter- and intramolecular conformational effects caused by changing the degree of ionization and/or the counter-ions affect the apparent net polyelectrolyte charge and the cation binding.[15-20] The validity of such proposals must be evaluated if the role of humics in aqueous geochemical systems is to be understood.

The relative aromatic versus aliphatic content of humics and fulvics has been a topic of considerable discussion.[1,3,21-23] This has led to controversy as to whether polymaleic or polyacrylic acids can be used as satisfactory models for humics. The available spectroscopic and other analytical data on humics and fulvics seem to confirm that aliphatic carboxylate, aromatic carboxylate, phenolic, and other sites are active in binding metals. The high carboxylate content

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of PMA and PAA have made them attractive model compounds.

In this work, direct spectroscopic comparative studies have been performed on PMA, PAA, fulvic, and humic acids. Using laser Raman spectroscopy, conformational changes in PMA are reported as a function of the solution pH. Nuclear magnetic resonance (^{13}C, NMR) and Fourier-transform infrared (FTIR) spectra were obtained for solid samples of PMA, PAA, fulvic and humic acids. Turbidity measurements were made on solutions of PMA and PAA as a function of pH. All of these confirm the importance of conformational changes for these complexation agents. The possible effects of these changes on their chemical and physical interactions and, in particular on metal binding are discussed.

EXPERIMENTAL

Polymaleic anhydride and polyacrylic acid were obtained from Polysciences, Inc. Polymaleic acid was produced from the base hydrolysis of the polymaleic anhydride and purified by recrystallization at a pH of 4 in an ice bath. Humic and fulvic acid samples were obtained from Lake Bradford, Florida using methods described previously[21]

Infra-red spectra were obtained using KBr pellets on a Fourier-transform infrared spectrometer (Mattson, Cygnus-100) at a resolution of 2 cm^{-1} The Raman instrumentation used in this work has been described in detail previously[25] Spectra were taken at 2 cm^{-1} on aqueous solutions in standard 1 cm pathlength cuvettes. Nuclear magnetic resonance spectra were obtained on solid samples with magic angle spinning techniques. A Bruker 200 MHz ^{13}C spectrometer was used to measure the spectra

Turbidity measurements were made using standard water quality turbidity instrumentation (DRT Turbidimeter, HF Scientific Model DRT 100). Formazin standards were used to calibrate

the instrumentation. The results are reported in nephelometric turbidity units (NTUs) Hydrogen ion concentrations were varied by addition of reagent grade solutions of HCl or NaOH and high purity (Nano-pure) deionized water

RESULTS

During these initial studies, it was discovered that when adjusting the pH of concentrated solutions of PMA to ca 4 caused precipitation of PMA The crystals were observed to be needle-like and white, whereas the initial solutions of PMA produced from the basic hydrolysis of polymaleic anhydride were colored. The coloration ranged from yellow to brown, and depended upon the lot number of the original polymaleic anhydride. Fluorescence and visible spectroscopy of the initial PMA solutions and those made from the white crystals from the acidic precipitation showed less colored and fluorescent impurities in the latter, presumably reflecting the loss of aromatic substructures from the original anhydride sample At very low pH values (less than 1), PMA solutions were observed to form opalescent, colloidal suspensions

Concentrated solutions of PAA (approx 50mg/ml) were observed to coagulate over a broader range of pH downwards from about pH 5 No crystalline precipitate formed and large colloidal gel-like structures were present in acidic solutions (pH less than 1)

Nuclear Magnetic Resonance Spectra

Carbon-13 NMR spectra are presented in Figure 1 for unpurified PMA, purified PMA, and fulvic and humic acids Solid state C 13 NMR has been shown to be useful tool for characterization of the types of carbon atoms contained in fulvic and humic acids [21] The major carbon signals in the spectra are assigned as follows aromatic (130 ppm), carboxyl (175 ppm) unsubstituted aliphatic (0 50 ppm), methoxyl carbons (55 ppm), ether and carbohydrate car

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tions (60-72 ppm and 106 ppm), oxygen substituted aromatic phenolic carbons (150 ppm), and carbonyl carbons (180-200 ppm).[23] Aromaticity of the polymers (natural and synthetic) can be estimated by integrating the region between 100-160 ppm.[24] In agreement with the interpretation of the preceeding paragraph, the spectra of the purified PMA contains substantially less aromatic content than the unpurified material.

These spectra indicate that fulvic acids have more carbonyl carbons and less aromatic carbons than the humic acids. There has been some controversy on whether humics and fulvics contain aromatic substructures.[2,23] Our spectra clearly indicate that these fulvics and humics contain aromatic units; moreover, these vary in aromatic/aliphatic content depending upon the source of the material and its chemical and physical history.[23]

The non-aromatic nature of pure PMA is seen in these spectra, supporting the concern about its value as a model for the humic and fulvic acids.

Fourier-transform Infrared Spectra

Figure 2 shows the FTIR spectra for solid samples of PAA, purified PMA, the residual polymeric material left after separation of the PMA crystals, a fulvic acid, and humic acid The broad bands in the region between 2600 and 3500 wavenumbers are due to O-H and C-H stretches. The carboxylate C=O stretches are observed in the region between 1600 and 1750 cm.[2] The broad spectral feature around 1200 cm 1 and the peak observed near 3000 cm-1 are measures of the aromatic character of the polyelectrolytes.[2] The spectrum of the impurities from the PMA purification explains the earlier confusion where IR spectra were used to demonstrate that fulvic acids and PMA were very similar in structure. PMA with impurities present, would lead to a spectra reflecting some aromatic character similar to that obtained from natural fulvics

In the PAA spectrum, the bands between 600 and 1000 cm−1 can be attributed to C-H bending in the olefi.. - linkages.[?] The band between 600 and 700 wavenumbers is a measure of the cis-structures, while the shoulder at 900 cm−· is due to the trans-isomers. The relative band strengths are consistent with the PAA being predominantly in the trans-conformation as would be expected from the entropy effects and relative stabilities of the cis- and trans-isomers.[·]

Laser Raman Spectra

Laser Raman spectra of aqueous PMA solutions were taken as a function of pH to examine directly the conformational change in solution. The spectra are given in Figure 3. At pH greater than 7, only one carboxylate frequency was observed (1650 cm−1), and, consistent with the symmetric nature of the carboxylate anion, was observed to give a strong signal. Other bands were observed at 1400, 1300, and 1175 cm−· due to C-C and C-O functionalities. As the pH was lowered, two distinct C=0 stretches are observed between 1600 and 1700 cm−· (see figure 3). As well, the other Raman features in the region of 1300 and 1175 cm−· were lost from the spectrum. The peak at 1400 cm · shifted slightly to lower wavenumbers and broadened. These results are interpreted as being consistent with formation of an intermolecular hydrogen bonded structure for PMA in the region of pH 4-5.

Turbidity Measurements

Highly concentrated solutions of PAA (40 mg/ml) and PMA (70 mg/ml) were titrated and the turbidity (nepheolometric turbidity units, NTUs) of the solutions determined as a function of pH. The results are given in Table 1. In the case of PAA, the solutions were observed to become colloidal at low pH while PMA was found to form crystals in a narrow pH range near 4 5

DISCUSSION

The NMR and FTIR spectra for PAA, PMA, fulvic and humic acids show considerable differences in the relative amounts of aromatic and aliphatic carbons and in the carboxylate concentrations (in meq g), between the natural and synthetic polymers. It is also apparent that the purity of the synthetic polymers needs to be assured when studying these polyelectrolytes as "model" systems

An examination of the structure of PMA shows that the addition of one hydrogen to the carboxylate structures should lead readily to internal hydrogen bonding between adjacent carboxylates. The resulting loss of flexibility and localized effective charge density effects its ability to remain in solution or to bind cations. This accounts for the precipitation of PMA as a crystaline material in a narrow pH range corresponding to 50 percent ionization of the carboxylate groups. The intramolecular hydrogen bonding can occur in PMA can occur in PMA because of the free rotation around the aliphatic C-C bond in this synthetic polymer. By contrast, in PAA the olefinic bonds lead to sufficient steric effects to minimize this type of interaction and subsequent effects upon metal binding

The turbidity data shows that for PMA, the dissolution phenomenon has a very sharp onset. Again PAA differs with the turbidity increasing over a larger pH range. The fact that PAA does not crystalize, but forms colloidal gels at low pH suggests that intramolecular bonding is not as important as in the case of PMA. Indeed the observations are more consistent with molecules of PAA binding via intermolecular hydrogen bonding

The laser Raman study of PMA confirms that there are two types of carboxylate groups for the purified PMA which is not fully ionized. This confirms the value of Raman spectroscopy to study directly the conformational behavior of polyelectrolytes in aqueous solutions. Further

studies with other counter-ions are planned to directly evaluate the conformational effects as a function of ion type and size. This data will help to finally resolve many of the discrepancies in the literature regarding the interactions of polyelectrolytes with metals and other ions.

Are PMA or PAA "good models" for fulvic or humic acid systems? The FTIR and NMR spectra show that fulvics and particularly humics are quite aromatic in contrast to the pure PMA and PMA model systems. The spectral studies presented her indicate that aliphatic polyelectrolytes may be more conformationally flexible, when compared to aromatic systems. Perhaps co-polymers with aromatic units would better mimic fulvic and/or humic acid systems. Whatever model compounds are used, prior characterization of the polyelectrolyte should include NMR, FTIR, and Raman spectroscopies. The presence of impurities in solution may be responsible for many of the discrepancies in the literature regarding the results of potentiometric titrations of the synthetic polyelectrolytes. We have shown that as one removes the aromatic impurities the PMA spectra and its potentiometric begavior are significantly altered.

CONCLUSIONS

We conclude that conformational changes in aqueous solutions of natural polyelectrolytes in their binding of cations is important when developing chemical models which attempt to describe aqueous geochemical systems satisfactorily

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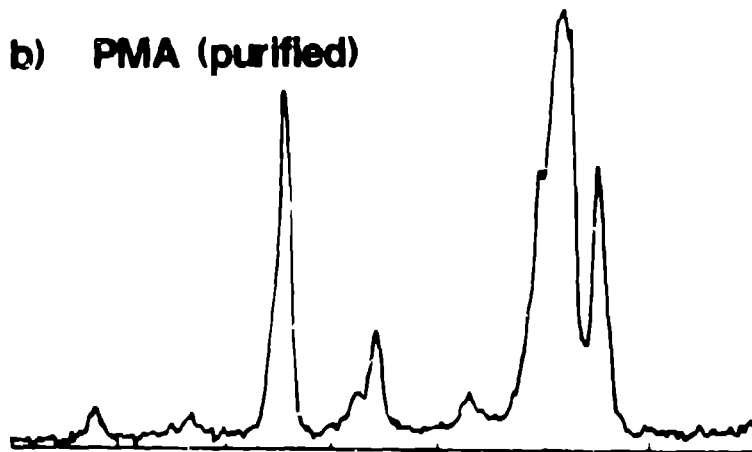
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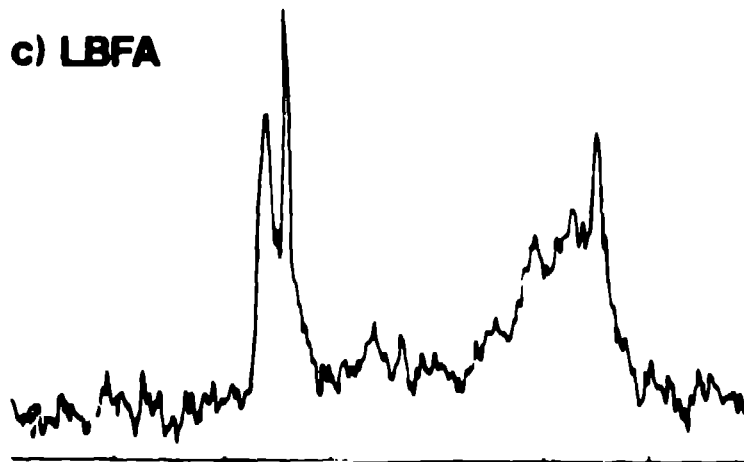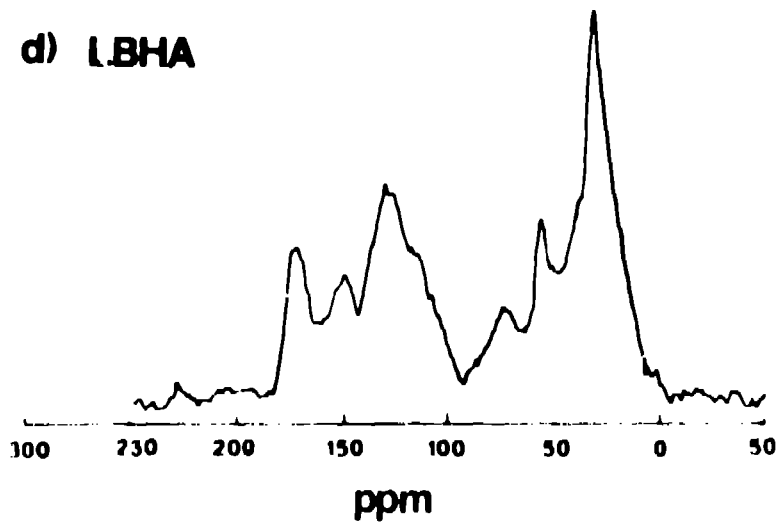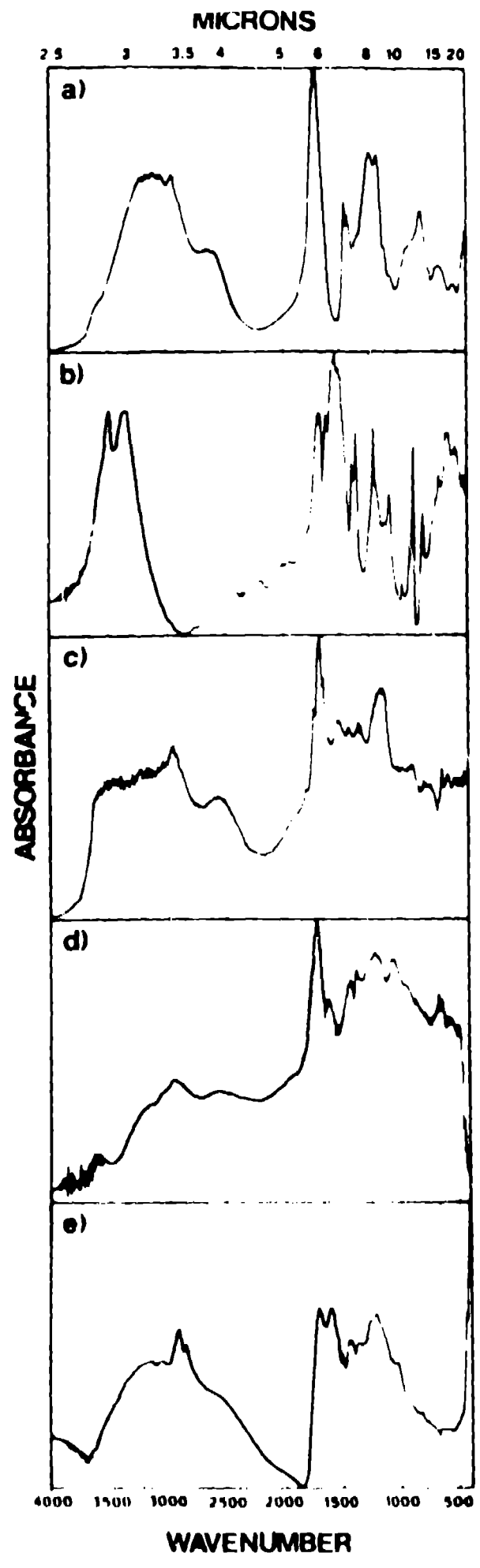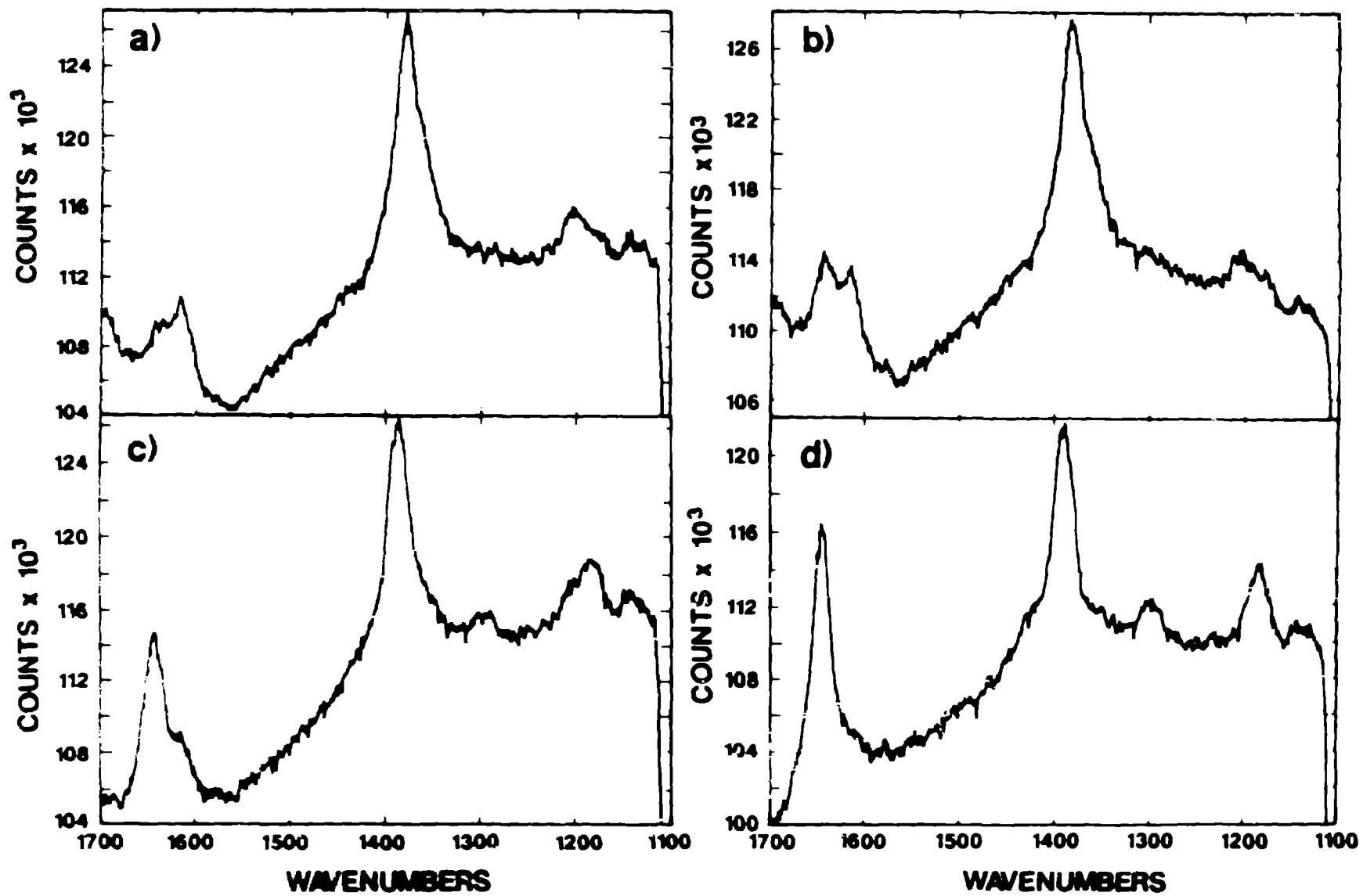
a) PMA (unpurified)
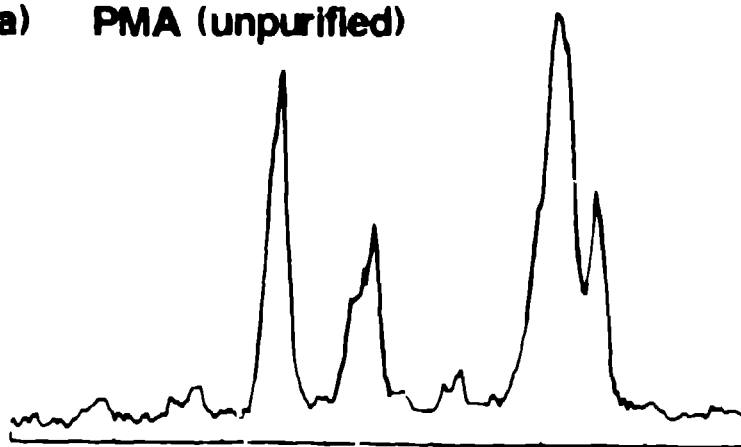
b) PMA (purified)

c) LBFA

d) LBHA

300 230 200 150 100 50 0 50

ppm

Figure III

FIGURE CAPTIONS.

Figure 1. Solid ^{13}C NMR spectra for a) unpurified PMA, b) purified PMA, c) fulvic acid, and d) humic acid. Aromatic carbons are in the region of 100-160 ppm, peaking at 130 ppm. Carboxylate carbons are at 175 ppm (See text for other assignments). Note the significant loss of aromatic structures in the PMA that has undergone acidic precipitation and purification.

Figure 2. Fourier-transform infrared (FTIR) spectra taken for a) PAA, b) purified PMA, c) the residual colored impure polymeric material left in solution after acidic precipitation of the PMA, d) fulvic, and e) humic acids.

Figure 3. Laser Raman aqueous solution spectra of purified PMA as a function of pH. a) pH 4, b) pH 5, c) pH 6, and d) pH 7. Note the clearly identified $C=O$ stretches for the two types of carboxylate groups between 1600-1700 cm^{-1}, and their changing relative contributions as a function of pH indicating intramolecular hydrogen bonding.

TABLE 1. Turbidity of concentrated solutions of PAA and PMA as a function of pH. Turbidity is reported as nephelometric turbidity units (NTUs).

| | PAA | PMA |
	(40 mg/ml)	(70 mg/ml)
pH	**Turbidity (NTUs)**	**Turbidity (NTUs)**
14.0	6.2	10
8.2	6.8	-
7.0	-	10
6.0	7.8	10
5 0	12	10
4.5	14	18
4 0	24	25
3.5	-	25
3 0	22	-
2.0	14	20
1 0	-	16