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FROM ENHANCED OIL RECOVERY OIL-IN-WATER EMULSIONS

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OCTOBER 1986

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERP/ERL 86-88 (J)

This work was supported in part by the Federal Panel on Energy
R+D (PERD)

ERP/ERL 86-88 (J)

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ABSTRACT

Emulsion from an enhanced oil recovery process has been treated by ultrafiltration with three types of membranes. Permeation of the aqueous phase through membranes led to the separation of the emulsion. It is believed that the permeates contain surface active components that were responsible for the stability of the emulsions. These components were characterized by Fourier transform infrared spectroscopy and Inductively coupled plasma. Analysis showed that the surfactants were carboxylate molecules bearing hydroxyl groups. These components were similar to some fulvic and humic acid samples that were isolated from soils. Potential for reinjection of this material into oil wells with steam is discussed.

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CARACTERISATION DES SURFACTANTS ISOLES PAR ULTRAFILTRATION DES
EMULSIONS HUILE/EAU PRODUITES LORS DE LA RECUPERATION ASSISTEE
DU PETROLE

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RÉSUMÉ

Une émulsion produite lors des opérations de récupération assistée d'huiles lourdes a été traitée par ultrafiltration à l'aide de trois différentes membranes. Dans chaque cas, la perméation de la phase aqueuse a permis la séparation de l'émulsion. Il en a été déduit que le perméat contient des composés tensio-actifs responsables de la stabilité des émulsions. Ces composés ont été caractérisés par spectrométrie infra-rouge à transformée de Fourier (FTIR) et par plasma induit (ICP). Les analyses montrent que ces surfactants sont des carboxylates portant des groupements hydroxyles. Ces composés sont similaires à certains acides humiques et fulviques présents dans les sols. La réinjection potentielle de ces surfactants dans les puits en même temps que la vapeur est discutée.

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INTRODUCTION

In Western Canada, large deposits of heavy oil and bitumen remain to be exploited because of their low demand by refiners and the economics of their recovery. However, as supplies of light crudes are being consumed, more commercial scale heavy oil recovery sites may become operational. The current trend for enhanced oil recovery (EOR) in this region is the use of steam floods, cyclic steam injection, and fire flooding of the reservoir. The operations that use steam require large volumes of water of sufficient quality for steam generation and the current supply of high quality surface water will be well taxed by future development (1). This will require the recycling of, water from producing wells (produced water) for steam generation.

Typically, produced water has low levels of heavy oil and bitumen and is in the form of stable oil-in-water (O/W) emulsion. Before it can be fed to the steam generators used in the field, produced water must be cleaned of any remaining oil, treated to remove silica, and softened to remove hardness. Current treatment of these emulsions includes the use of induced gas flotation, sand filtration, hot lime softening, and strong and weak cation exchange, while other treatments such as pressurized filtration and wet air combustion have been studied (1-5). Although membrane separations have been considered for the treatment of produced water, problems such as fouling and thermal degradation of the membranes have discouraged their application. Ultrafiltration has been successfully used in our laboratory for the production of an oil-free permeate water of very high quality (6,7). These studies have shown that while the permeate is oil-free, it does contain other components that exhibit surface properties such as supporting a foam. Further, some of the emulsions that were processed by ultrafiltration separated into oil rich and oil lean phases, in excess of the amount of heavy oil that would be liberated by the dewatering of the emulsion (6-8). It is considered that the membranes selectively permeated emulsion stabilizing agents and this accounts for the destabilizing of these emulsions.

This work deals with the characterization of the stabilizing agent that has been removed from the emulsion in the membrane permeate using membranes of different materials. Fourier transform infrared spectroscopy (FTIR) and Inductively coupled plasma (ICP) were used to characterize the organic and inorganic components of differently treated samples. The infrared spectra of the organic components were compared with those of other materials that are similar in nature.

EXPERIMENTAL

The emulsion sample was a wellhead bitumen/water/mineral emulsion (approximately 4% bitumen) kindly supplied by Texaco Canada Resources Ltd., from a steam flood in situ pilot plant

at Fort McMurray, Alberta (Athabasca region). Presumably, this emulsion has not been treated with demulsification agents, though the absence of free oil suggests that the emulsion had been skimmed. There was little evidence of settled solids. The emulsion sample was stored at room temperature in a plastic container prior to use and was not pre-treated in any manner.

To prepare the membrane permeate for analysis, the bitumen and solids were removed by permeation through three membranes. The first was a Nylon-66 membrane of $0.1\ \mu\text{m}$ nominal pore size (Pall). This membrane had the lowest permeation rate despite its large pore size and high pressures had to be used (8000 kPa compared to 700 kPa for the others). This can be attributed to fouling of the membrane by bitumen. The other two were cellulose ester membranes: cellulose nitrate of $0.01\ \mu\text{m}$ pore size (Schleicher and Schuell) and cellulose acetate fabricated in-house by methods capable of producing membranes with NaCl separation in excess of 80%. The cellulose acetate membrane is considered to be a reverse osmosis membrane with small pores while the other two are considered as ultrafiltration membranes with large pores and little NaCl separation.

The membrane permeation experiments were performed by placing approximately 150 mL of emulsion into an unstirred 90 mm diameter membrane holder and pressurizing with nitrogen gas to induce permeation. The permeate was collected in water cooled containers to prevent evaporation losses. Prior to analysis, the samples were stored in a refrigerator at 0°C .

The permeates in 10mL portions were separated and analyzed according to the characterization scheme shown in Fig. 1. Upon acidification, a dark solid precipitated and was separated by centrifugation at 2500 rpm for 1 h. The supernate, precipitate and permeate from each membrane were then frozen in preparation for freeze drying which was performed using a Labconco Freeze Dryer 3 unit. Freeze drying of permeates and precipitates yielded a brown solid while the dried supernate was almost white although the supernate itself was slightly coloured. This is attributed to the large concentration of salts in the supernate. One of the supernates (from the cellulose nitrate membrane) was also extracted with ethyl acetate to compare the composition of the remaining organic components with the corresponding precipitate and permeate. Solvent from the extract was gently evaporated and the remaining sample was dissolved in water and freeze-dried.

Inductively coupled plasma (ICP) was used to assess the composition of the salts isolated in the supernates using a Jarrell-Ash ICAP 9000 with a cross-flow nebulizer suitable for high salt concentrations.

RESULTS AND DISCUSSION

FTIR spectra of the permeates are shown in Fig. 2. As can be seen, permeates obtained with the three membranes are very similar. Peaks at $2910\text{-}2960\ \text{cm}^{-1}$ are characteristic of aliphatic CH stretching. No unique bands for aromatics are

prominent which indicates low aromatic content. This is confirmed by the ultraviolet (UV) spectra of the raw permeates that did not show any significant absorbance in the 200-300 nm region. The broad absorption band centered in the region of 3400 cm^{-1} is characteristic of OH stretching from alcohols. Hydroxyl absorption from acids usually located between 2900 and 3300 cm^{-1} could not be observed in the permeates. The strong absorption band at 1120 cm^{-1} is also due to hydroxyl groups (CO stretching). The combination of two strong bands at 3400 and 1120 cm^{-1} without noticeable absorption in the 1200 - 1300 cm^{-1} region may be an indication that these are primary alcohols. The two strong absorption bands located at 1400 and 1580 cm^{-1} are characteristic of carboxylates and correlate with the low absorption in the 2900 - 3000 cm^{-1} region (COOH).

The presence of carboxylates is also confirmed upon acidification of the raw permeates at pH 2. Under these conditions, a precipitate appeared which was separated by centrifugation. Infrared spectra of these precipitates (Fig. 3) show the appearance of the characteristic carboxylic absorption at 1710 cm^{-1} and broadening of the OH stretching absorption down to the 2800 cm^{-1} (COOH) region. Thus, the main functionalities in the precipitate are carboxylic acids (from the transformation of carboxylates) and alcohols. However, the relative intensity of the alcohol bands at 1120 cm^{-1} is much smaller indicating that a significant portion of the compounds bearing alcoholic hydroxyl groups remains in the supernate. Absorption bands also appeared between 1400 and 1450 cm^{-1} due to the absence of carboxylate absorption. These could be caused by hydrocarbon absorption (to agree with the 2850 - 3000 cm^{-1} aliphatic absorption) or bicarbonates that have co-precipitated with the organic acids. The broad absorption at about 1240 cm^{-1} is probably due to hydroxyl groups of the carboxylic acids.

After separation of the precipitate, the supernate was also freeze-dried and analyzed by FTIR. ICP was also used in order to identify the nature of the inorganic constituents of the permeate. Again, all supernate infrared spectra show much similarity (Fig. 4). Some of the peaks present in this fraction were already identified in the precipitates or raw permeates. The very broad hydroxyl absorption between 3000 and 3500 cm^{-1} reveals the presence of both alcohols and acids. Inorganic anions could also be identified by FTIR. Since the hydrocarbons are very weak, the 1400 - 1500 cm^{-1} band is probably due to carbonates. This appears to be confirmed by the presence of a peak at 860 cm^{-1} . The peak located at 1120 cm^{-1} appears to be very strong compared to the 3400 cm^{-1} band. This may indicate a contribution from sulfate ions on top of hydroxyl absorption which seems to be confirmed by a 460 cm^{-1} band. The presence of sulphur is also confirmed by ICP analysis (Table 1) which revealed a sulphur concentration in the range of 5 to 6% in the solids isolated from the supernate. The ICP analysis is useful in indicating which cations are present in the supernates. It appears that the main cation is sodium which accounts for more than 20% of the total weight of the supernate

solids. It is not really possible to know which cation is involved in the carboxylate formation with the acids isolated in the precipitate. However, since sodium is present in such a high quantity, it is the most logical candidate although other cations might also be involved in the formation of carboxylates (9). The supernates were expected to be highly concentrated in inorganic salts, but the high concentrations of barium, strontium and iron were not anticipated. This ICP analysis is not exhaustive and other elements might also be present as has been emphasized by Kotlyar et al. (10) who examined Athabasca oil sands.

Finally, one supernate was extracted with ethyl acetate, after removal of the precipitate. Upon extraction, most of the colour was transferred to the organic phase. The concentration of material left after solvent evaporation was not calculated but was visually less than that of the precipitate. The infrared spectrum is very similar to the precipitate's (Figure 5). Thus the insoluble and soluble organic materials present in the acidified permeate are very similar.

The precipitate, raw permeate and supernate infrared spectra were compared with those of acidic components of oil and soil that are believed to have surface properties. These components are naphthenic acids (Eastman-Kodak), and humic and fulvic acids isolated from two different soils, i.e., Bainsville clay (Ottawa) and Armadale soil (Prince Edward Island) (11,12). As can be seen in Fig. 6, the naphthenic acid spectrum does not approach any of the spectra of the different fractions isolated from the permeates. The main differences are the absence of the absorption band at 3400 cm^{-1} (hydroxyl groups from alcohols) and the difference in bands located between 1000 and 1400 cm^{-1} . Also, the higher absorbance of aliphatic peaks ($2800-3000\text{ cm}^{-1}$) relative to the broad hydroxyl band ($3000-3200\text{ cm}^{-1}$) indicates a lower hydroxyl/carbon ratio in the naphthenic acids. The carbonyl peak is much sharper in the naphthenic acids. This might indicate lower molecular weight material (naphthenic acids are liquid while our samples were all solids) and/or a more homogeneous structure. However, comparisons of the precipitates with humic and fulvic acids (Fig. 7) showed some interesting similarities, especially in the case of the Armadale fulvic acids. Fulvic acids are not well defined molecules, but they are generally believed to be mixed alcoholic-carboxylic acid type molecules which could contain heteroatoms (13). However, it must be noted that fulvic acids are usually defined as components that do not precipitate upon acidification while the precipitate is defined as humic acids. Nevertheless, there is no sharp division between the two types of molecules and fulvic acids are sometimes regarded as being simple representatives of humic acids. Both are the major constituents of the "humic substances" present in soil samples. Their presence in heavy oils is not unexpected since they are believed to be precursors of coals (14,15). Our results strongly indicate that the emulsion stabilizing surfactants isolated in this work are related to humic substances.

Concentration of isolated surfactants was in the range of 500 ppm for this particular sample but no effort was made to measure it accurately. Since significant amounts of these surface active substances could be isolated, there is a potential for their reinjection along with the steam in the oil well. Injection of humic acids and treated lignites has already been proposed (16) and carboxylate (both aliphatic and aromatic) surfactants have been investigated for their potential use in enhanced oil recovery (17,18). Since the isolated surfactants in this study are related to humic acids and carboxylates, they would combine the surfactant potential of both. The emulsion treatment process could begin with membrane separation of inorganic salts and surfactants, after which the latter could be recovered for reinjection into the oil reservoir.

CONCLUSION

Surface active components present in enhanced oil recovery oil/water emulsions and isolated in the membrane permeates have been identified as carboxylates from acidic material that are similar to some fulvic acids, instead of naphthenic acids as could be expected. Like the fulvic acids, there is no major contribution of aromatic carbons and the acidity comes from both carboxylic acids and alcohols as indicated by the infrared spectra. The carboxylates are believed to be in the sodium form as sodium is by far the most concentrated cation identified by ICP. Other cations such as calcium, iron and to a lesser extent magnesium, barium, strontium, potassium, and nickel have also been detected by ICP indicating that the permeates are a mixture of inorganic salts and water-soluble carboxylate molecules bearing hydroxyl groups. These carboxylate surfactants could be considered for reinjection in the oil well to improve oil recovery in the same way that commercial surfactants are used in some recovery projects.

ACKNOWLEDGEMENT

The authors wish to acknowledge the technical assistance of E. Bonvie and T. Moher and the support of Dr. C.M. Preston for supplying samples of fulvic and humic acids.

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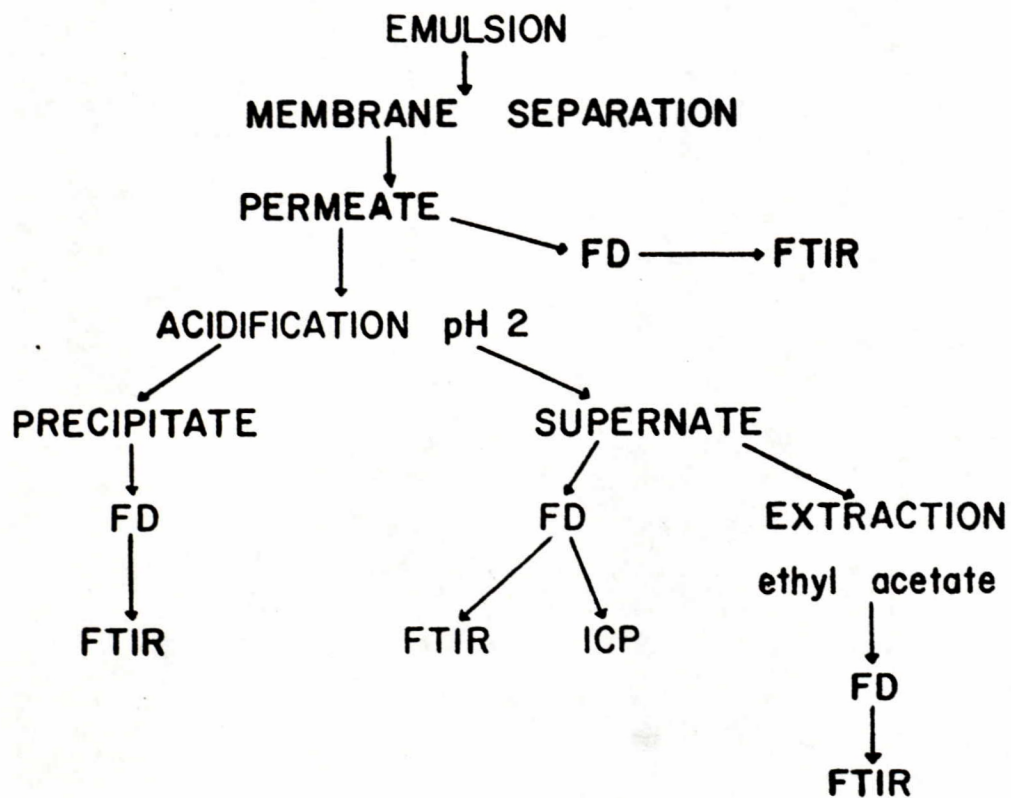
FIGURE CAPTIONS

- Fig.1- Sample preparation and analysis scheme.
- Fig.2- FTIR spectra of freeze-dried permeates obtained with three membranes: NY - Nylon-66; CA - Cellulose acetate; CN - Cellulose nitrate. (KBr pellets)
- Fig.3- FTIR spectra of freeze-dried precipitates isolated from the three permeates: NY - Nylon-66; CA - Cellulose acetate; CN - Cellulose nitrate. (KBr pellets)
- Fig.4- FTIR spectra of freeze-dried supernates isolated from the three permeates: NY - Nylon-66; CA - Cellulose acetate; CN - Cellulose nitrate. (KBr pellets)
- Fig.5- Comparison of FTIR spectra of freeze-dried samples of cellulose nitrate permeate and its three isolated subfractions.
- Fig.6- FTIR spectra of commercial naphthenic acid from Eastman-Kodak. (Diluted in CCl_4)
- Fig.7- FTIR spectra of humic materials isolated from two soil samples. (KBr pellets)

Table 1 - Concentration of various elements in the supernates
as determined by ICP

Element	Concentration in freeze-dried supernates (ppm)			Concentration in permeates (ppm)		
	CA	CN	NY	CA	CN	NY
Na	210,000	222,000	230,000	119.7	193.1	188.6
S	25,700	22,000	24,600	14.65	19.14	20.17
Ca	13,400	7,600	7,000	7.64	6.61	5.74
Fe	4,800	2,500	4,900	2.74	2.18	4.02
K	3,600	4,200	4,500	2.05	3.65	3.69
Ba	1,700	1,000	1,000	0.97	0.87	0.82
Sr	900	500	500	0.51	0.44	0.41
Mg	900	600	300	0.51	0.52	0.25
Ni	800	400	2,000	0.46	0.35	1.64
Mn	0	50	3,700	0.00	0.04	3.03

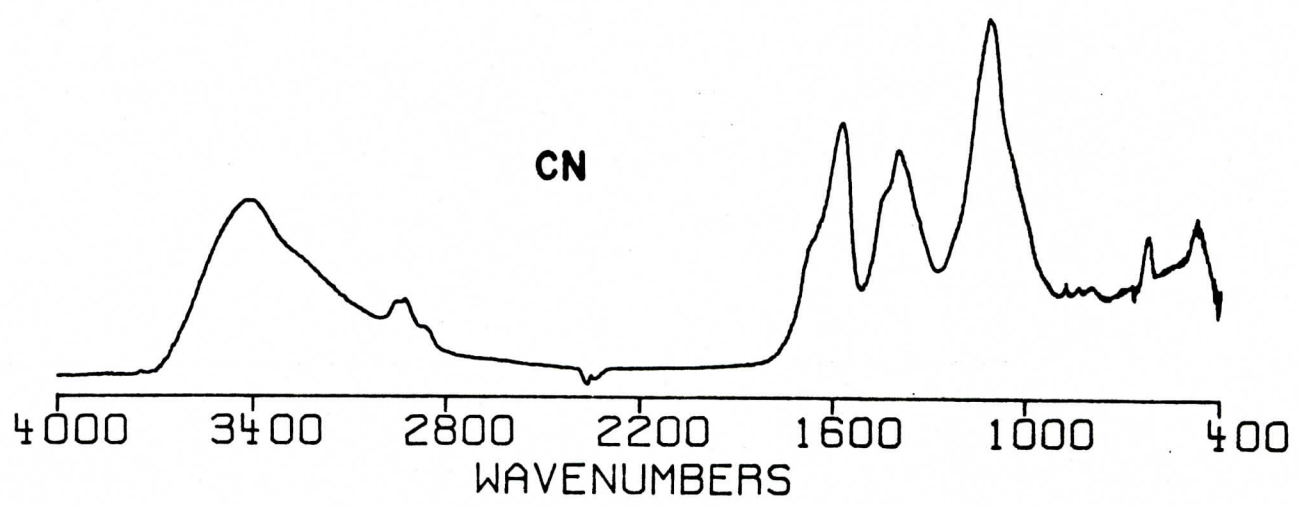
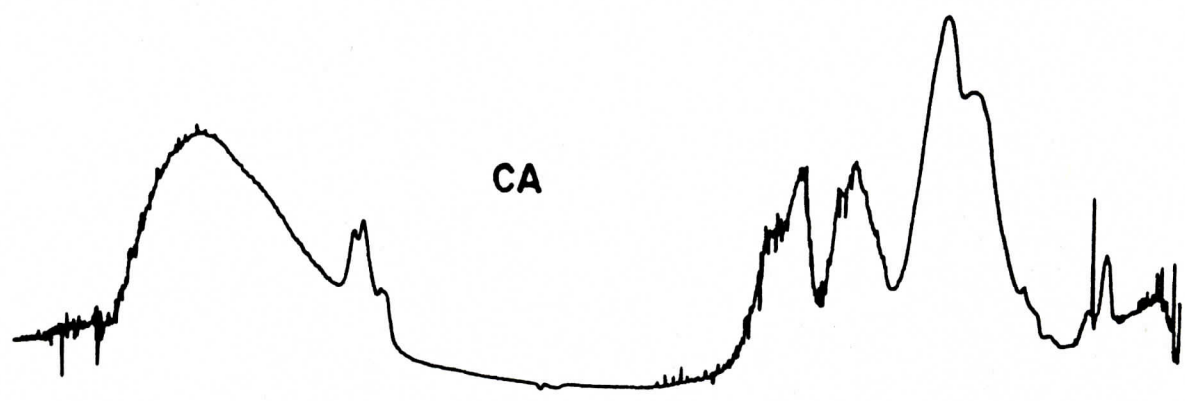
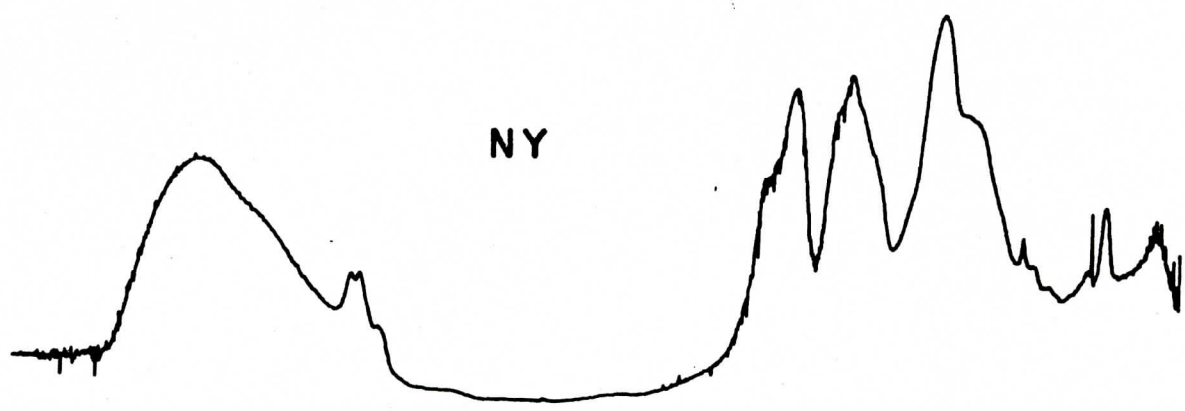
Si, Al, Ti, P, V = 0
CA = Cellulose acetate
CN = Cellulose nitrate
NY = Nylon-66



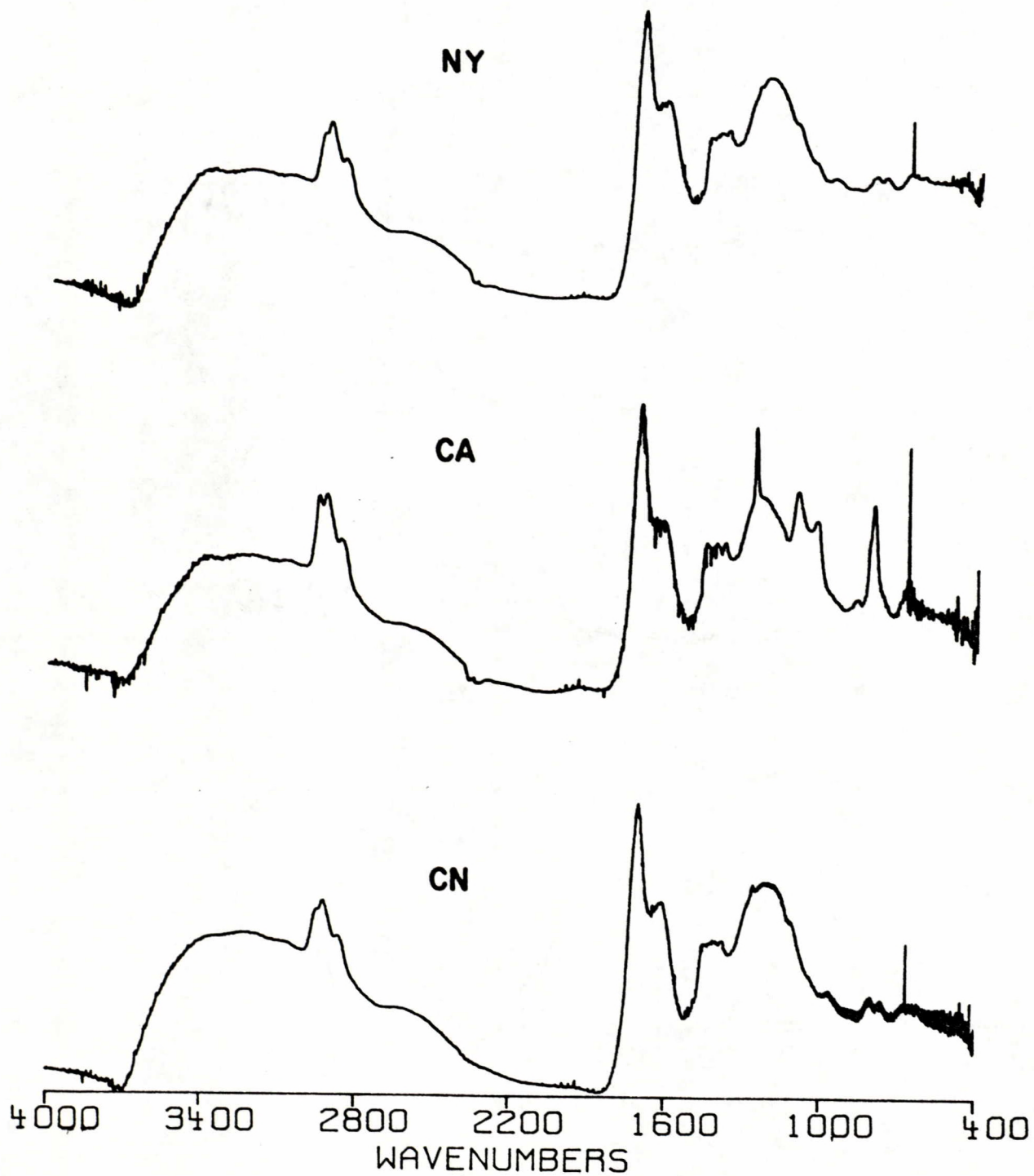
FD = FREEZE - DRYING

FTIR = FOURIER TRANSFORM INFRARED

ICP = INDUCTIVELY COUPLED PLASMA

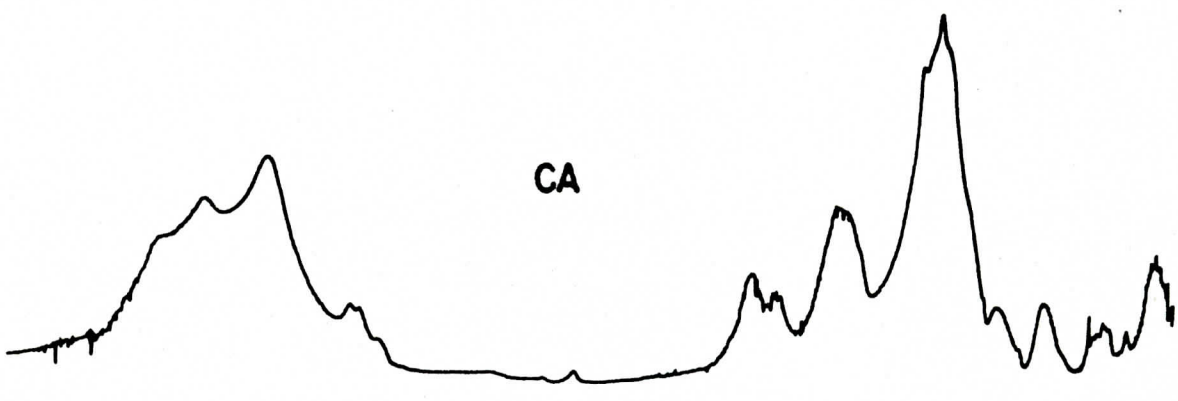


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WAVENUMBERS

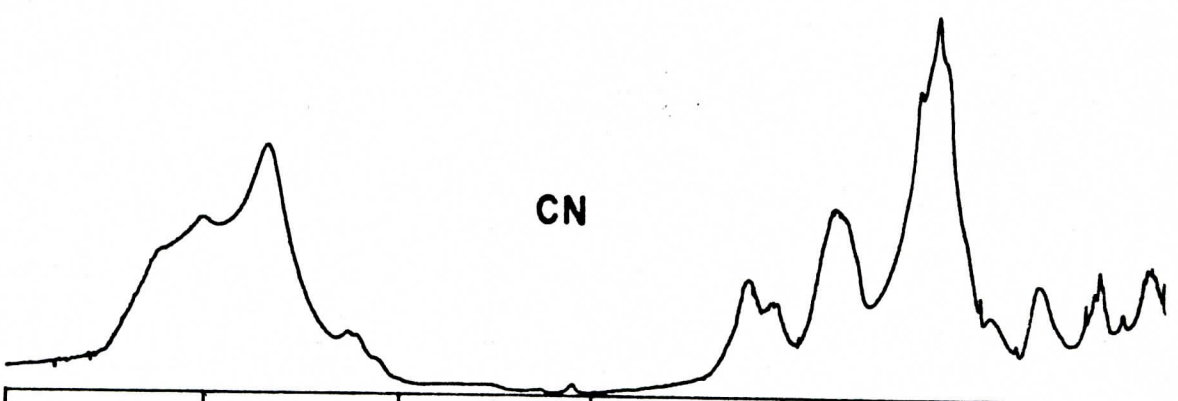




NY

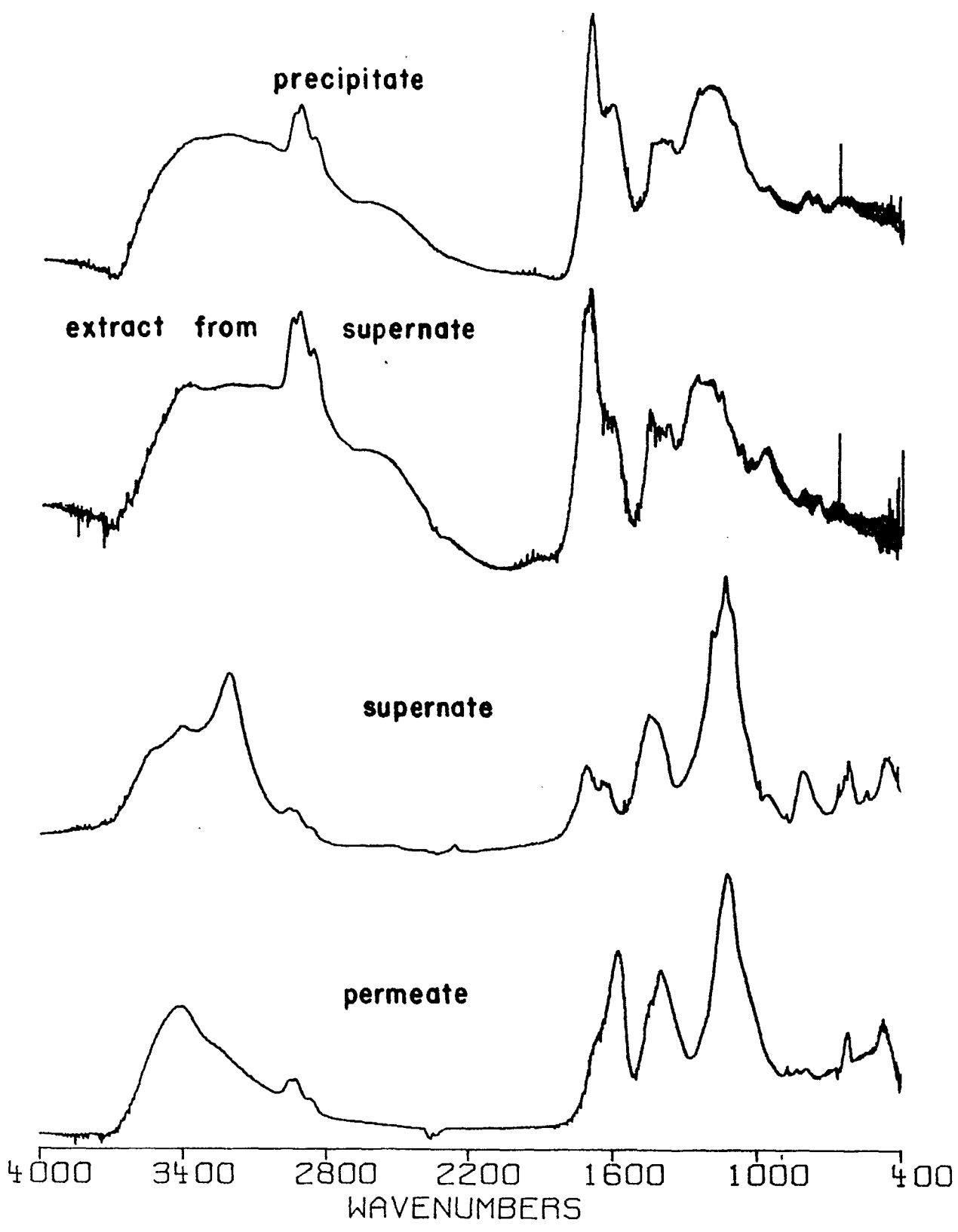


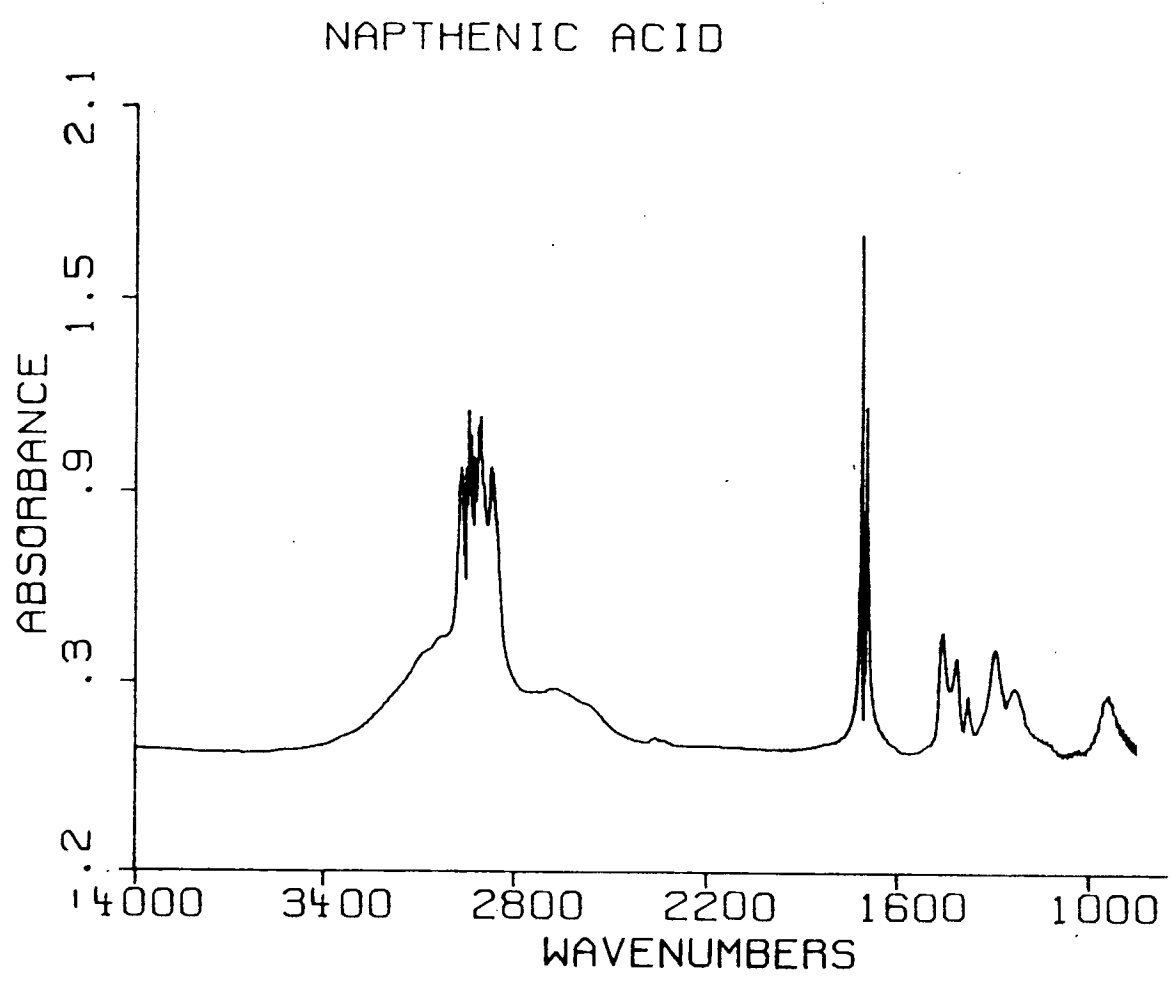
CA



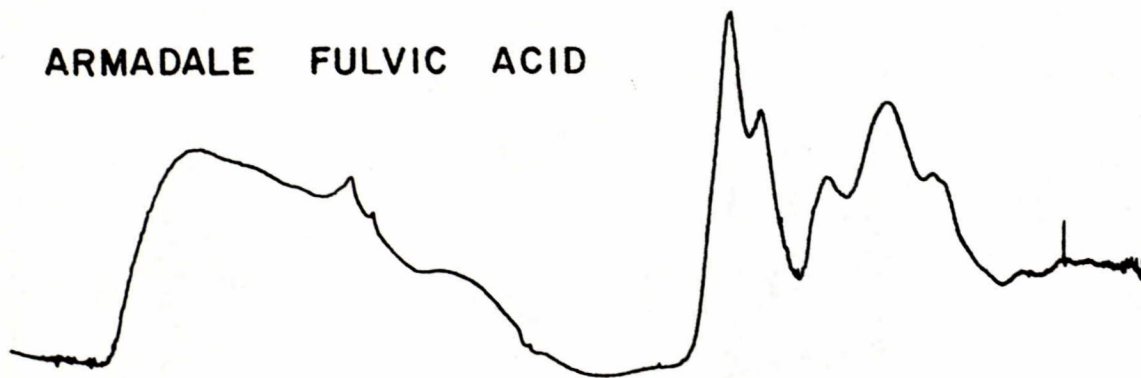
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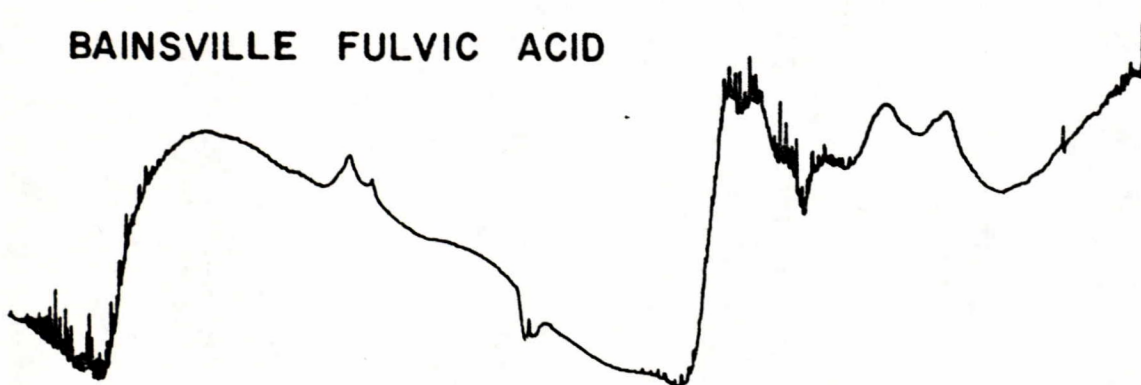




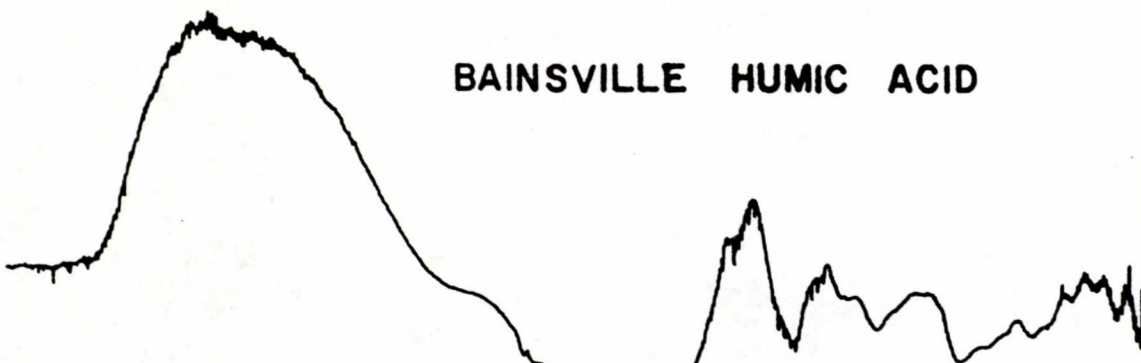
ARMADALE FULVIC ACID



BAINSVILLE FULVIC ACID



BAINSVILLE HUMIC ACID



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WAVENUMBERS