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MASTER

HYDROGEN BONDING IN ASPHALTENES AND COAL

Quarterly Report for January 1,1979 - March 31,1979

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DISCLAIMER

OBJECTIVE AND SCOPE OF WORK

The objective of this program is to investigate the nature and strength of hydrogen bonding and other molecular interactions that occur in asphaltenes and coal-liquids, and to seek possible correlations with the viscosity of the product oil. During the period January 1,1979 - March 31,1979, the paper "Viscosity, Calorimetric, and Proton Magnetic Resonance Studies on Coal Liquid Fractions in Solution," by K. C. Tewari, N. S. Kan, D. M. Susco, and N. C. Li, appeared in Anal. Chem., Vol. 51, pages 182-185, 1979.

We have completed a manuscript for the Division of Fuel Chemistry Preprint, ACS Washington, DC meeting, September 1,1979. The manuscript is as follows:

Characterization of Upgraded Coal Liquids

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INTRODUCTION

The upgrading of coal liquids has become necessary in order to make acceptable fuels for home, transportation and industrial use. Several research groups have stepped up their activities in coal liquid upgrading, as evidenced by a recent symposium (1). However, only a few studies have been reported on characterization and structural analysis of the different fractions obtained in the upgrading of coal-derived liquids.

In this study, upgraded coal liquids from a blend of 30 weight percent of SRC I with 70 weight percent of SRC II, as well as from SRC II, have been studied by IR and NMR techniques. The variation of structural parameters of the upgraded liquids has been determined as a function of reaction temperature and contact time in the catalytic hydroprocessing. The results indicate that along with the decrease in heteroatom contents, asphaltene content, aromatic content and a corresponding increase in aliphatic content, the hydrogen-bonded structure and phenolic OH content of the coal liquids drastically decrease with increase in contact time and temperature. The disappearance of phenolic OH in upgrading process follows a first-order kinetics but no such dependence was observed in case of acidic NH.

EXPERIMENTAL

SRC I and SRC II were made from Kentucky bituminous coal. SRC II was a liquid product with initial boiling point of 453 K and extending into end boiling point of 665K. Elemental analysis of the two products are listed in Table 1, with the results of solvent fractionation based on solubility in toluene and pentane. The blend was prepared by adding 30 parts SRC I to 70 parts SRC II by weight at 413-423 K for 2.5 hrs. under nitrogen pressure.

SRC II and the blend were hydroprocessed over a Ni-Mo catalyst (Nalco NM504) in a trickle bed reactor at hydrogen pressure of 13.8 MPa, liquid hourly space velocities (LHSV) of 0.5, 0.75, and 1.0 hr^{-1}, and temperatures of 672 and 694 K. Prior to the hydroprocessing, the catalyst in the oxide form was presulfided with a H_2/H_2S stream. The hydroprocessing experiments were carried out during a 32-hour continuous operation.

Infrared spectra were recorded on solutions in CS_2 in a 5-mm KBr liquid cell with the solvent in the compensating beam on a Beckman IR-20 infrared spectrometer. The NMR structural parameters (2) were determined before and after hydroprocessing by using a 60-MHz FT NMR spectrometer (Perkin-Elmer R-600).

RESULTS AND DISCUSSION

Several properties, including the results of elemental analysis and solvent analysis for the two kinds of feed materials and their upgraded liquids, are listed in Table 2. The blend and SRC II are sometimes referred as F-1 and F-2, respectively. Hydroprocessed liquids from F-1 are referred as U-1 to U-4, while the upgraded liquid from F-2 is referred as U-5, according to the various hydroprocessing reaction conditions as shown in Table 2. With F-1 as feedstock, increase in the H/C ratio is found with increase in contact time at 672 K, but a satisfactory increase in H/C can be obtained at higher temperature of 694 K. Values of H/C and specific gravity of U-5 are comparable to those of light petroleum crude oils such as Kirkuk and Khafji (H/C: 1.68-1.80; specific gravity: 0.85-0.89). Values of U-4 are comparable to heavy petroleum crude oils such as Eocene and Boscan (H/C ratio: 1.51; specific gravity: 0.95 - 0.99 (3). N/C ratio decreases with increase in contact time and temperature.

The IR spectra of F-1 and U-4 are shown in Fig. 1. The decrease of hydrogen-bonded structure after upgrading is seen by the dramatic decrease of broad bands of 3400 cm^{-1} (bonded OH) and 1610 cm^{-1} for U-4. The intense band of 1610 cm^{-1} for F-1 is due to the hydrogen-bonded carbonyl stretching in addition to the skeleton vibration of the aromatic ring (4).

Structural parameters were determined from NMR spectra of the coal liquids in CS_2. There seems to be no significant difference in the parameters of F-1 and F-2. (Table 3). It should be noted, however, that the CS_2 -soluble fraction of the blend (F-1) is 89.5% and that the toluene-insoluble fraction of F-1 could not be dissolved in CS_2. In using F-1 as feedstock, there is a gradual decrease in f_a accompanied by an increase in the degree of substitution of aromatic nucleus (σ), with increase in contact time of hydroprocessing at 672 K. At the higher temperature of 694 K, f_a of the upgraded oils from F-1 and F-2 were decreased to 0.33 and 0.17, respectively. Table 3 shows that U-5 is mainly composed of aliphatic compounds, and this is supported by the high H/C ratio (Table 2) as well as IR spectra.

Removal of phenolic OH and acidic NH groups in hydroprocessing of SRC liquids was studied kinetically by measuring the intensity of free OH and NH stretching vibrations at 3600 and 3480 cm^{-1}, respectively. The relative decrease of the OH and NH group intensities is summarized in Table 4 in relation to the contact time of hydroprocessing of F-1 at 672 K. The removal of OH group was found to follow first-order kinetics (Fig. 2). However, no such dependence was observed for the NH group. It must be mentioned that the importance of the effect of mass transfer processes or incomplete catalyst wetting has not been considered in this discussion. As shown in Fig. 2, the relative decrease in the N/C ratio also follows a first-order kinetics under the same reaction conditions. The relative reactivity of oxygen removal to nitrogen removal in hydroprocessing of F-1 at 672 K is estimated to be 2:1, from the slopes in Fig. 2.

Fig. 3 shows partial IR spectra of SRC liquids before and after hydroprocessing in rather concentrated CS_2 solutions of the same concentration (19.2 g/l). After hydroprocessing, the intensity of the 3600 cm^{-1} peak decreases and new absorption at 2670 cm^{-1} is found in the upgraded oils. The intensity increases with increase in contact time and temperature of hydroprocessing. The absorption in this region can be ascribed to the proton-transfer NH stretching (N^+ H...O^-) (5). We have previously found that when an aliphatic amine as triethylamine is added to the acid/neutral fraction of SRC process solvent, new absorptions were found at 2630, 2610 and 2505 cm^{-1} (6) and we ascribe these to the formation of proton-transfer ionic species, (N^+ H...O^-). The spectrum of U-5 shows that it contains a certain amount of such species, even after almost complete disappearance of NH stretching at 3480 cm^{-1}. The implication is that the proton-transfer ionic species are formed under present hydroprocessing conditions.

Table 5 gives the infrared absorbance ratio of CH_3/CH_2 for the hydroprocessed liquids in dilute CS_2 solution. The ratio decreases from 0.87 to 0.56 with increase in contact time of processing at 672 K, using F-1 as feedstock. The result may indicate that the upgraded oils in the hydroprocessing treatment takes on a saturated cyclic structure (7).

Structural parameters in the asphaltene fractions of the upgraded liquids are given in Table 6. It is interesting to note for the asphaltenes that the values of H_{au}/C_a actually decrease with increase in contact time of hydroprocessing, whereas the reverse is true for the unfractionated liquids. There is also an increase in the number-average molecular weight of the asphaltenes which are isolated from liquids which have been hydroprocessed with a longer contact time. The changes in properties of the various asphaltenes are particularly intriguing, and we plan further experiments with the asphaltenes.

Acknowledgments

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Table 1. Elemental and Solvent Analyses of SRC Products

SRC	Elemental Analysis (wt% maf) C	H	O	N	S	atomic H/C ratio	Solvent Fractionation Distribution (wt%) Toluene-insoluble (TI)	Asphaltene** (A)	Heavy Oil+ (HO)
SRC I	85.6	6.05	5.6*	2.01	0.74	0.84	34.1	48.8	17.1
SRC II	89.0	8.7	1.16	0.84	0.28	1.17	0.0	0.7	99.3

*by difference, **Toluene-soluble and pentane-insoluble, + pentane-soluble

Table 2. Properties of Hydroprocessed SRC Liquids

	Upgrading Conditions Temp. K	LHSV hr^{-1}	Elemental Analysis (wt% maf) C	H	O*	N	S	atomic H/C ratio	N/C $\times 10^2$	Solvent Fractionation TI	A	HO	Viscosity cp 311 K	Specific Gravity 289/289 K
F-1			87.9	7.95	2.5	1.32	0.3	1.09	1.3	10.2	18.5	71.3	120	1.068
U-1	672	1.0	88.9	9.7	0.7	0.61	<0.1	1.31	0.59	1.6	10.9	87.5	9.5	0.981
U-2	672	0.75	89.0	10.1	~0.3	0.50	<0.1	1.36	0.48	0.2	7.4	92.4	6.1	0.960
U-3	672	0.50	89.0	10.4	~0.2	0.24	<0.1	1.40	0.23	0.0	5.1	94.9	5.2	0.942
U-4	694	0.50	88.5	11.3	~0	0.16	0.017	1.53	0.15	0.0	0.5	99.5	3.0	0.899
F-2			89.0	8.7	1.16**	0.84	0.28	1.17	0.81	0.0	0.7	99.3	5.0	0.999
U-5	694	0.50	87.3	12.7	~0	0.02	<0.1	1.75	0.02	0.0	0.1	99.9	1.5	0.857

*by difference, **by direct method

Table 3. Structural Parameters for Hydroprocessed SRC Liquids

Sample	Proton Distribution (Area %) Aromatic H_a	Benzylic H_{α}	Aliphatic H_o	Structural Parameters f_a	σ	$H_{\sigma}/H_{\alpha} + 1$	H_{au}/C_a
F-1**	38.9	27.7	33.4	0.66	0.28	2.2	0.93
U-1	21.4	29.7	48.9	0.49	0.42	2.6	0.99
U-2	19.3	28.7	52.0	0.45	0.43	2.8	1.03
U-3	15.7	24.6	59.7	0.41	0.44	3.4	0.97
U-4	12.9	19.6	67.5	0.33	0.43	4.4	1.05
F-2	37.3	29.8	32.9	0.63	0.30	2.1	0.98
U-5	4.6	9.6	85.8	0.17	0.51	9.9	0.98

*Separation point between H_{α} and H_o chosen at $\delta = 2.1$ ppm

**Elemental analysis of the CS_2- soluble fraction of F-1: C 88.2, H 8.3, O 2.0, N 1.18, S 0.3. The CS_2- soluble fractions of F-1 and U-1 are 89.5% and 99.2%, respectively. All other samples are completely soluble in CS_2.

Table 4. Reduction of Phenolic (OH) and Acidic Nitrogen (NH) Groups in Hydroprocessing of the Blend of SRC I with SRC II

Sample	Unfractionated Liquid % OH*	% NH*
U-1	19	88
U-2	11	82
U-3	4.4	48

*% of original OH and NH groups remaining in the upgraded liquids, determined by IR.

Table 5. Infrared absorbance ratio of CH_3/CH_2 for various hydroprocessed SRC liquids.

Sample	F-1	U-1	U-2	U-3	U-4	F-2	U-5
A_{CH3}/A_{CH2}^*	0.87	0.62	0.59	0.56	0.57	0.83	0.53

*Absorbance of symmetrical stretching vibration of

CH_3 group at 2960 cm^{-1} : A_{CH3}
CH_2 group at 2925 cm^{-1} : A_{CH2}

Table 6. Structural parameters of asphaltene fractions isolated from upgraded SRC liquids.

Source of Asphaltene	Proton Distribution (Area%)			Structural Parameters				Mol. Wt.
	Aromatic	Benzylic	Aliphatic					
	Ha	H_α	Ho	fa	σ	$Ho/H_\alpha+1$	Hau/C_a	
F-1	37.9	38.1	24.0	0.76	0.40	1.6	0.64	820
U-1	33.9	36.0	30.1	0.75	0.39	1.8	0.57	1130
U-2	34.0	32.0	34.0	0.75	0.36	2.1	0.54	1180
U-3	34.0	32.5	33.5	0.75	0.36	2.0	0.54	1160

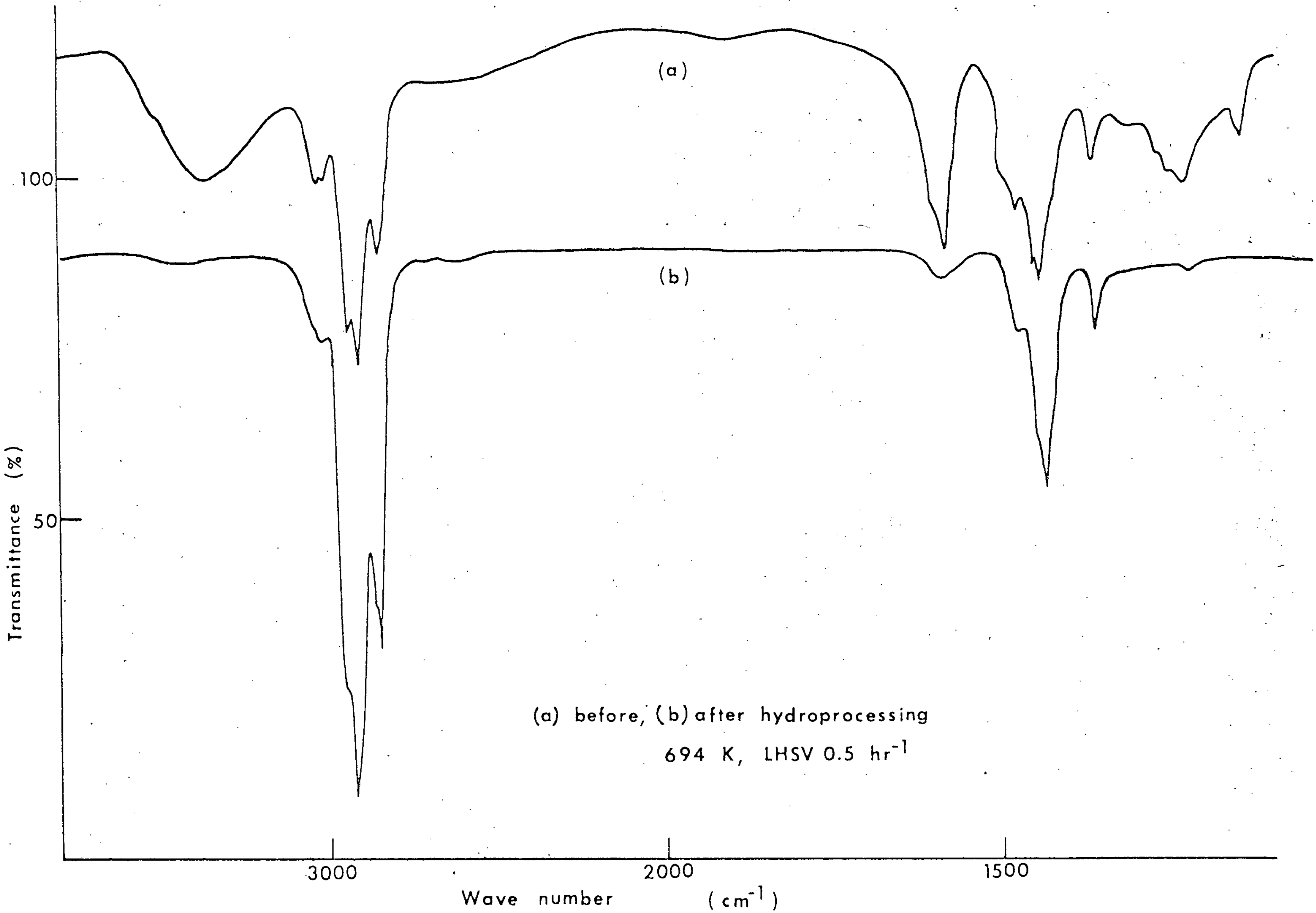


Fig. 1 IR spectra of the blend of SRC I with SRC II before and after upgrading

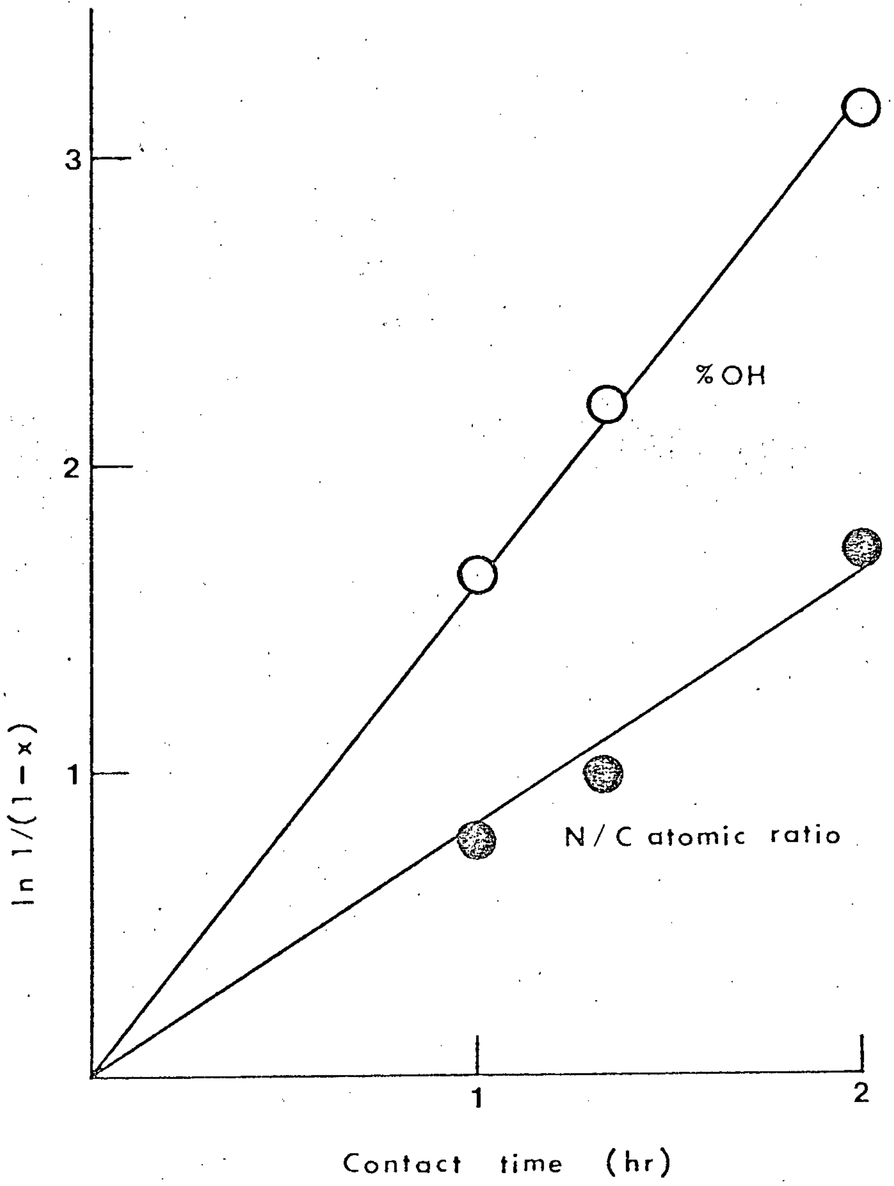


Fig. 2 First-order plot of removal of oxygen and nitrogen

Feed F−1, 672 K
x %conversion

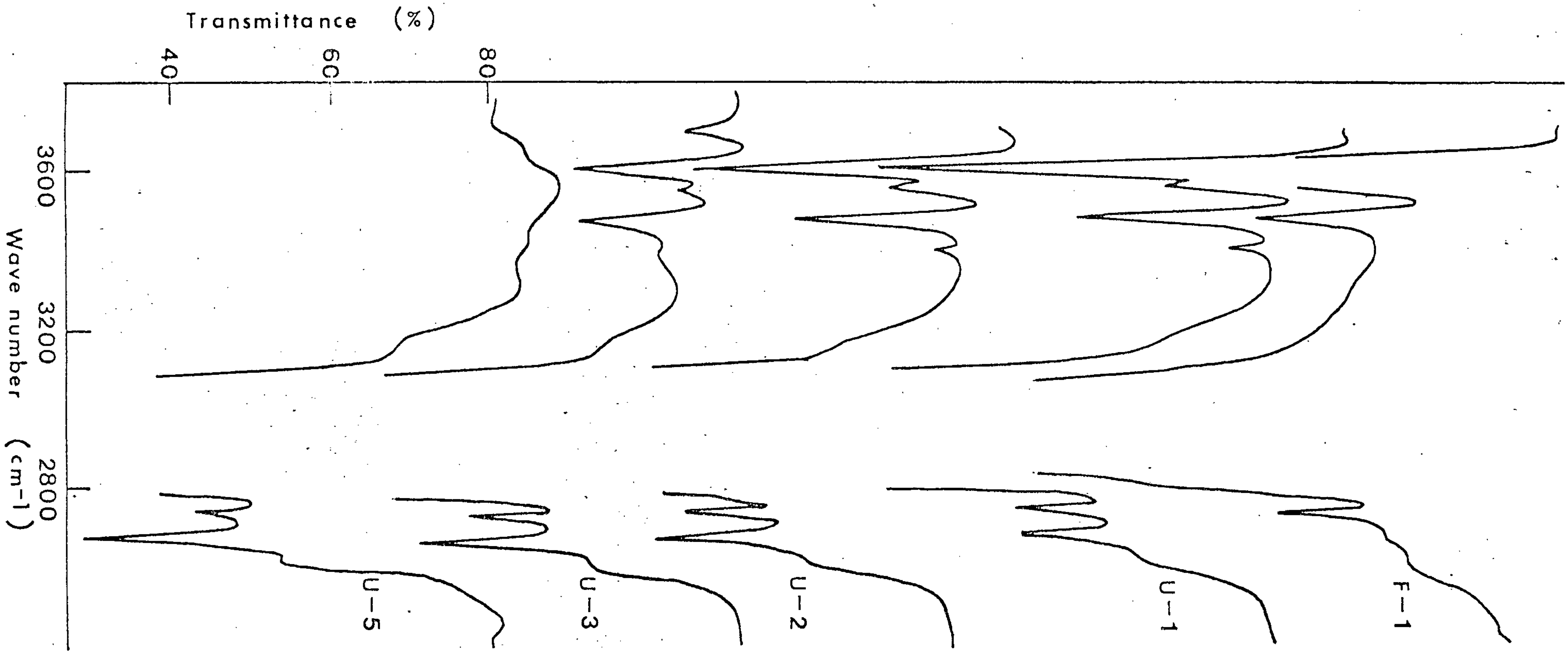


Fig. 3 Formation of proton transfer species (NH^+) in hydroprocessing

Solvent CS_2, 19.2 g/l

Preliminary Results on the Chromatographic Separation of SRC II and SRC II - Acid

The SRC II process solvent used in this study was prepared by Pittsburgh and Midway Coal Company from Kentucky #9 and #14 blend bituminous coal. The process solvent was separated into its acid/neutral and base components by bubbling dry hydrogen chloride gas through a stirred benzene solution, giving the weight ratio acid/base of 90.7/9.3. SRC II process solvent and its acid/neutral fraction are henceforth referred as SRC II and SRC II-Acid, respectively.

A Waters Associate Prep LC/System 500 with silica as the stationary phase was used to separate SRC II and SRC II-Acid into a number of fractions which differ mainly in their chemical properties. The fractionation was performed by a sequential elution by solvents through a silica gel column, and is described elsewhere (M. Farcasiu, Fuel 56, 9, 1977). The ratio of sample/silica gel was 1:80 (by weight). The elution solvents and the relative quantities of the fractions obtained are shown in Table I. The fractions separated by this method on a preparative scale were studied by NMR and IR Methods. The proton distribution of fraction 1-6 are shown in Table II.

Preliminary results of NMR and IR analyses indicate that fraction 1 obtained from SRC II and SRC II-Acid contains substantial amounts of aromatic hydrocarbons. IR spectrum of fraction 1 from SRC II-Acid shows a group of very intense bands at 1270, 1100 and 1050 cm^{-1} which may be assigned to aromatic oxygenated compounds such as aromatic ethers. (R.A. Friedel and J.A. Queiser, Anal. Chem. 28, 22 (1956).

Fractions 1 and 2 constitute two major fractions of SRC II and SRC II-Acid. Fraction 3 is a third major fraction of SRC-II Acid (ca. 22%). NMR spectrum of this fraction from SRC II-Acid shows distinct phenolic OH signal. The OH signal was found to be concentration-dependent in $CDCl_3$ solvent. The downfield shift of the OH signal with increasing concentration indicates association of molecules involving phenolic OH. Fraction 4 constitutes a third major fraction of SRC II. Fraction 4 of SRC II and fractions 4 and 5 of SRC II-Acid show distinct concentration-dependent phenolic OH-NMR signals in $CDCl_3$ solvent. The high yield of Fraction 5 from SRC II-Acid may be due to the di-and tri-phenols.

All fractions eluted up to this point are soluble in benzene. The wt % of Fraction 6 from both SRC II and SRC II-Acid is small and the material has limited solubility in $CDCl_3$ and C_6H_6.

For SRC II-Acid, the phenolic OH content increased with increasing fraction number (3,4,5), whereas for SRC II, only fraction 4 shows distinct phenolic - OH signal. The phenolic - OH signal at 6 ppm (for fraction 3 of SRC II-Acid) shifts downfield with increasing fraction number. The NMR spectra of SRC II, SRC II-Acid and their fractions are given in Figs. 1-12.

Further work on the characterization of the coal liquids and their fractions is in progress.

Table I

Fractions obtained by chromatography on silica gel (wt. %)

Fraction	Eluent	SRC II	SRC II-Acid
1	Hexane	20.5	29.1
2	Hexane/15% benzene	27.4	19.9
3	$CHCl_3$	9.0	21.9
4	$CHCl_3$/10% Et_2O	22.2	2.4
5	Et_2O/3% EtOH	5.6	16.4
6	Methanol	2.9	2.4
7	$CHCl_3$/3% EtOH	0.8	0.4
8	THF/3% EtOH	2.7	0.6
9	Pyridine/3% EtOH	0.9	0.6
10	Non-eluted	0.8	6.3

Table II

Proton distribution from NMR Data

Fraction	Aromatic H_a	Phenolic* H_{OH}	Benzylic** H_α	Aliphatic** H_o
SRC II	33.8	-	27.3	38.9
1	16.9	-	23.3	59.8
2	53.4	-	29.5	17.1
3	48.2	-	30.9	20.9
4	30.8	6.4	35.3	27.5
5	37.8	-	35.8	26.4
6	31.1	-	37.3	31.6
SRC II-Acid	33.0	-	26.8	40.2
1	22.3	-	25.3	52.4
2	54.6	-	28.7	16.7
3	33.7	6.4	31.8	28.1
4	41.4	7.6	32.2	18.7
5	37.3	8.5	28.1	26.1
6	22.2	-	30.7	47.1

* From the integrated intensity of observed OH signal

** Separation point between H_α and H_o chosen at 2 ppm from TMS

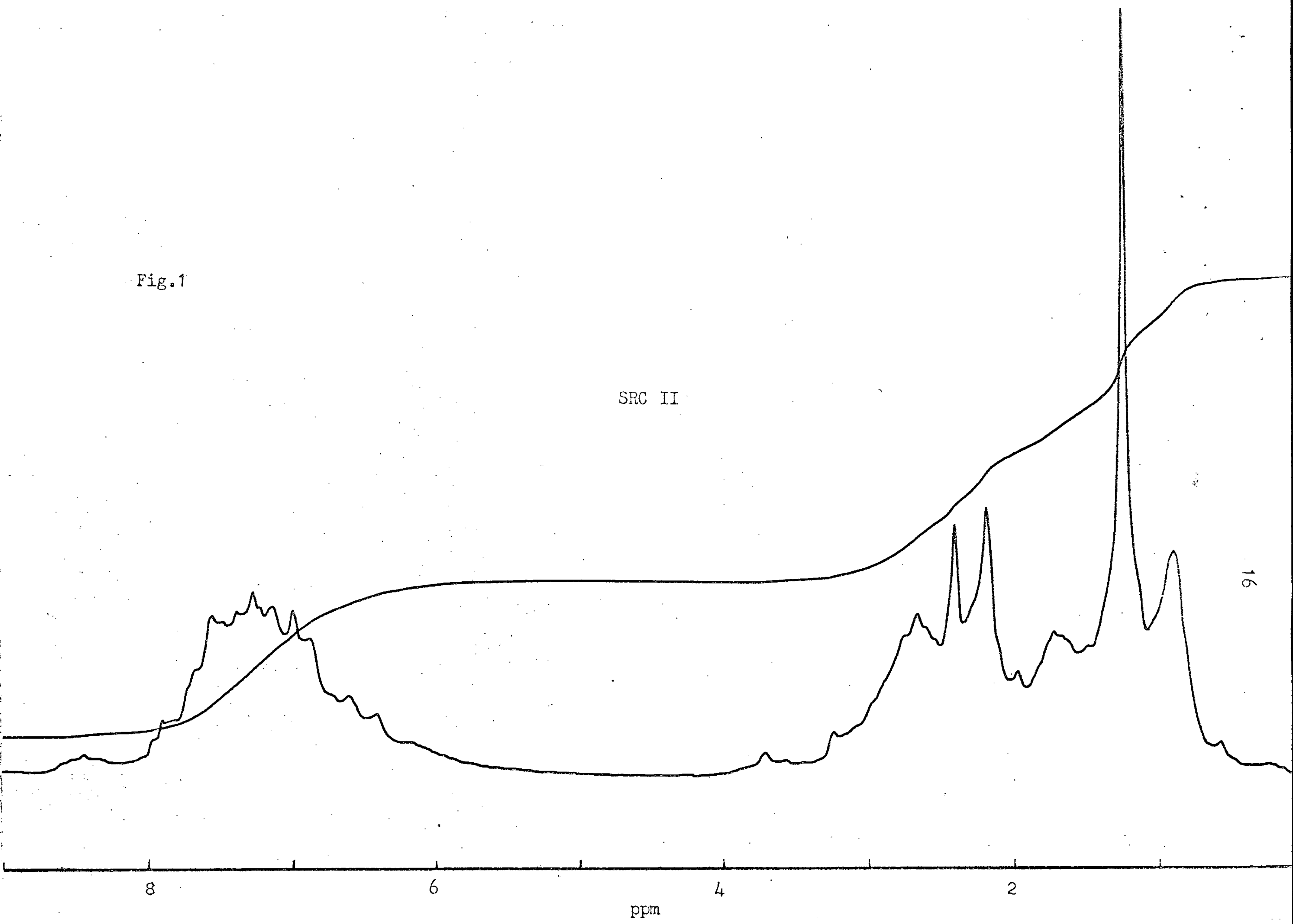


Fig.1

Fig.2

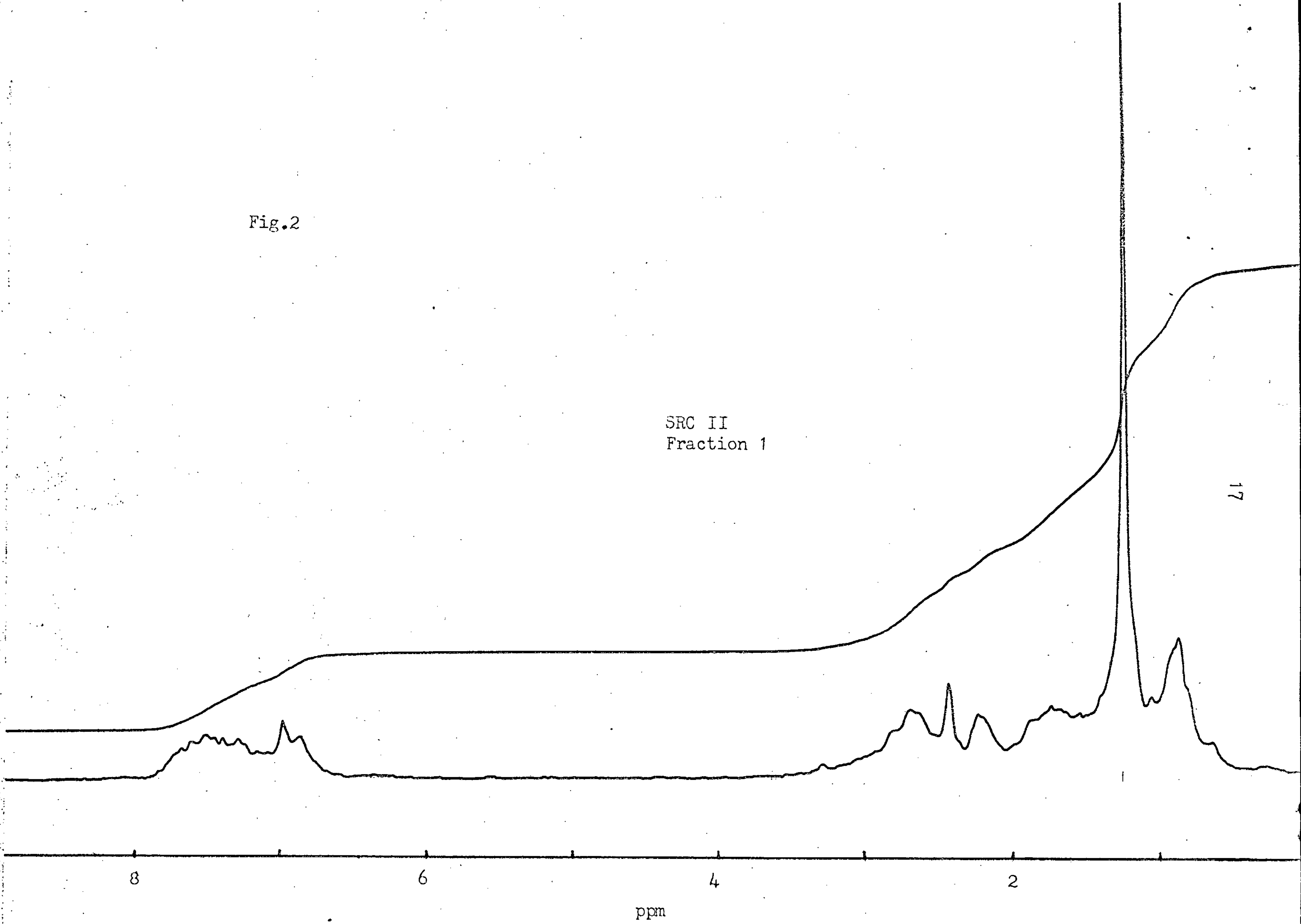


Fig.3

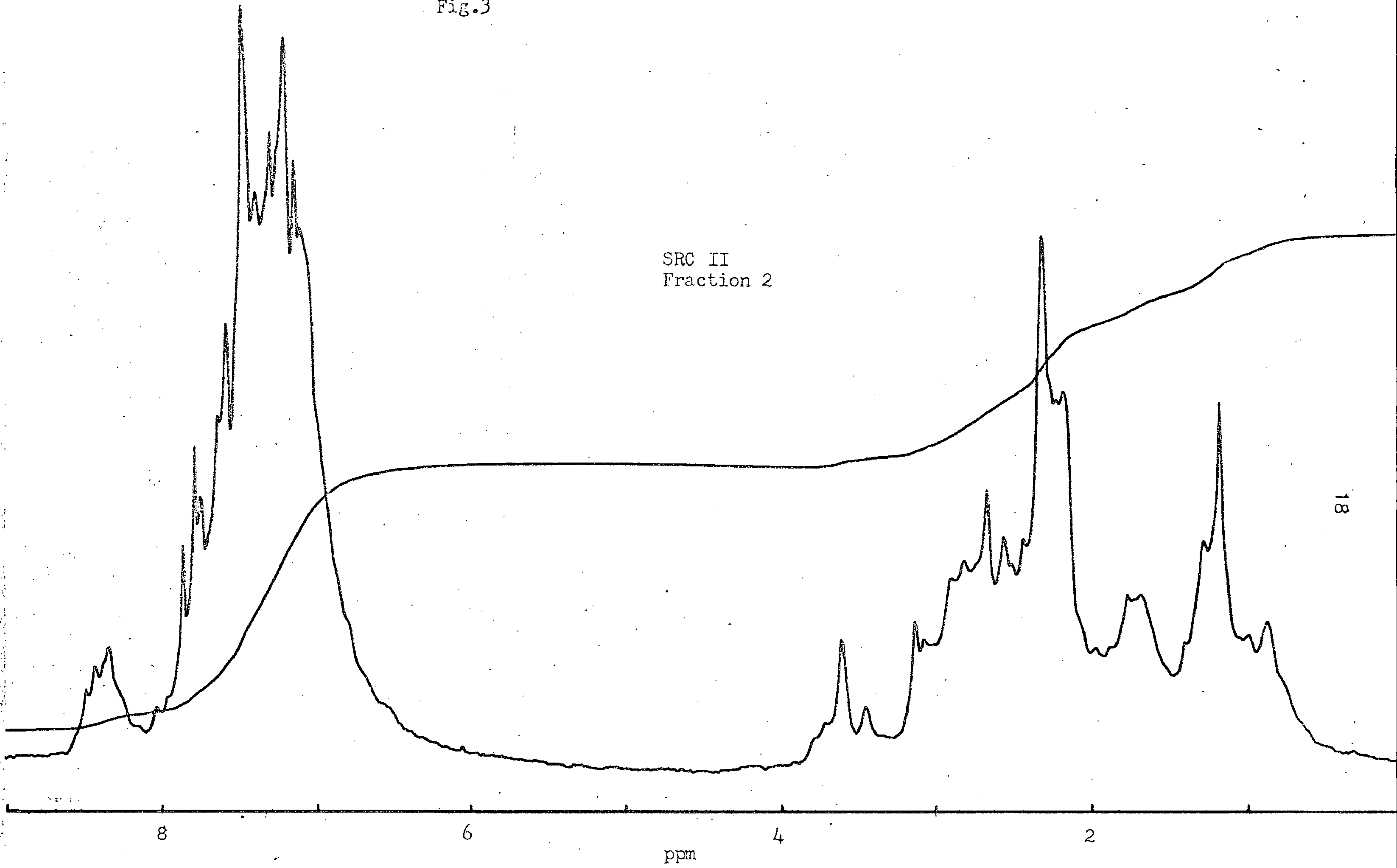


Fig.4

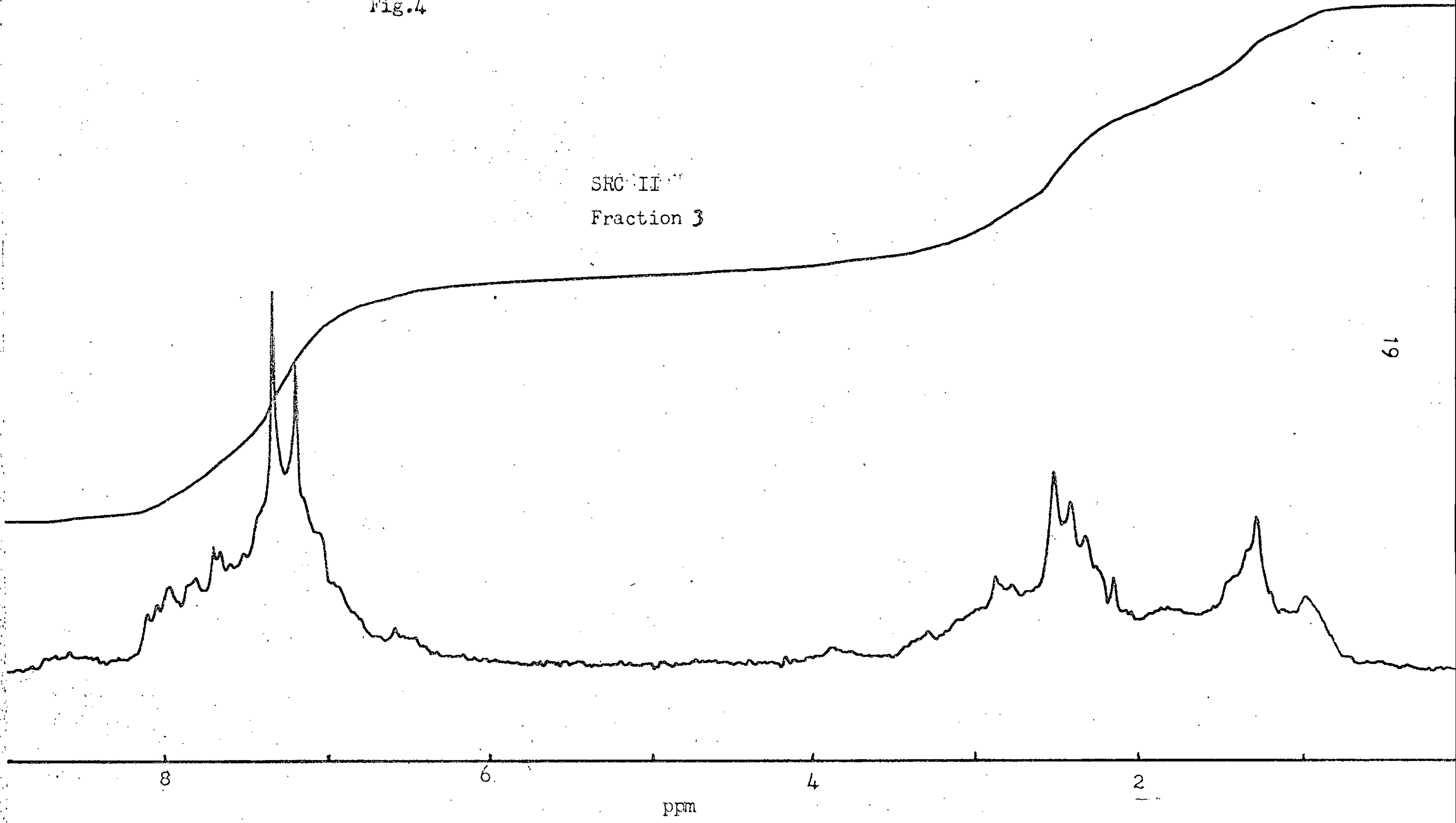


Fig.5

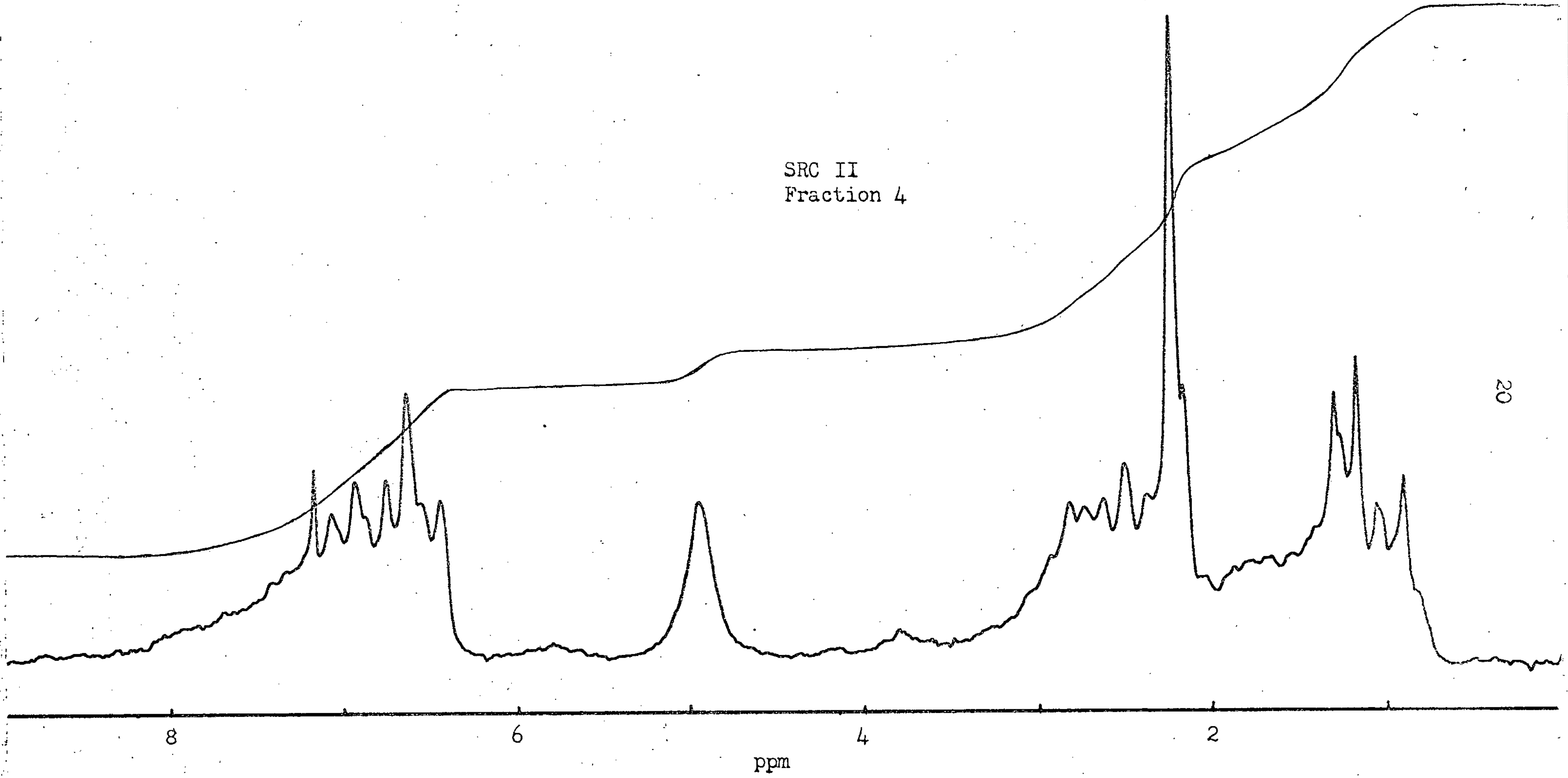


Fig.6

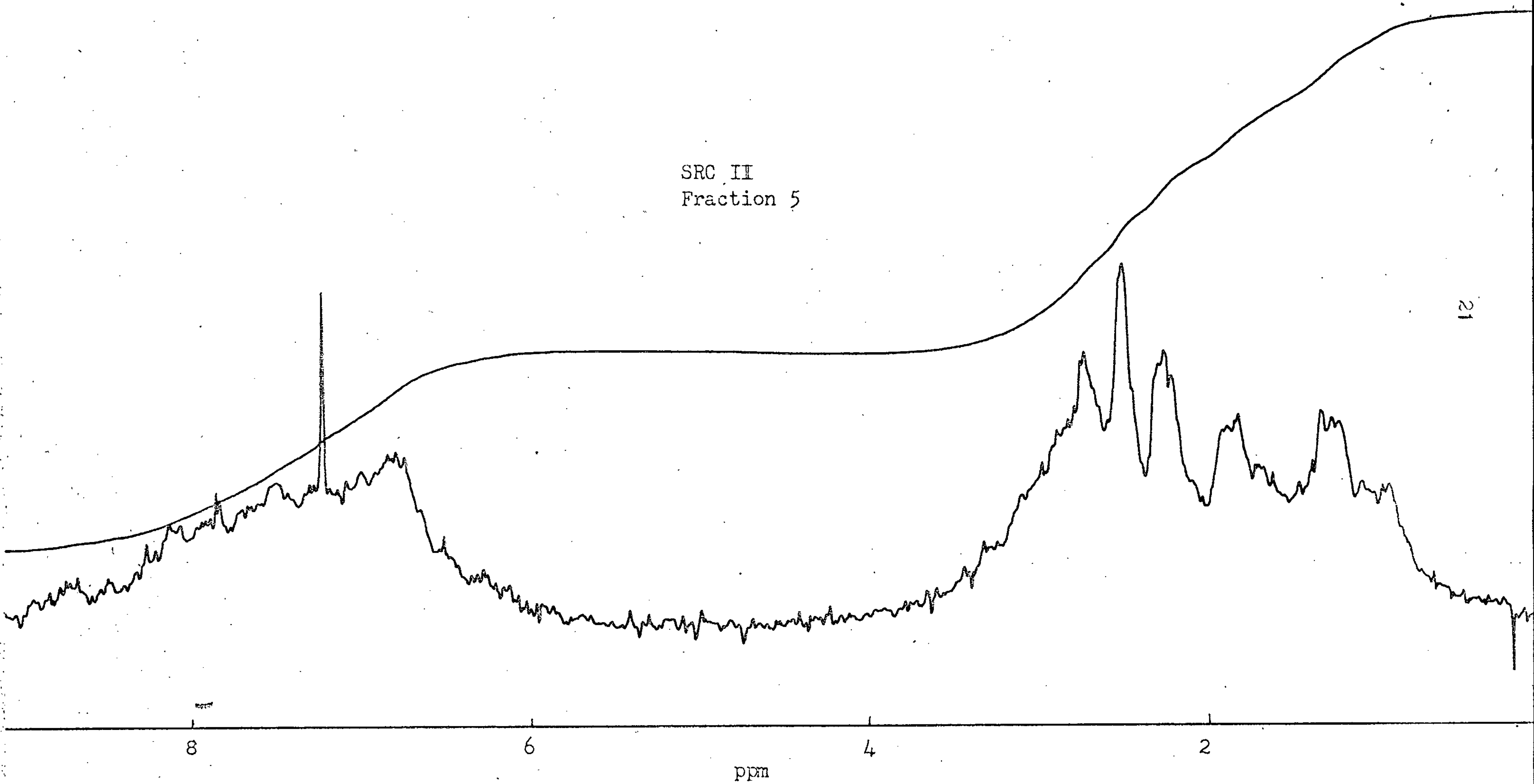


Fig.7

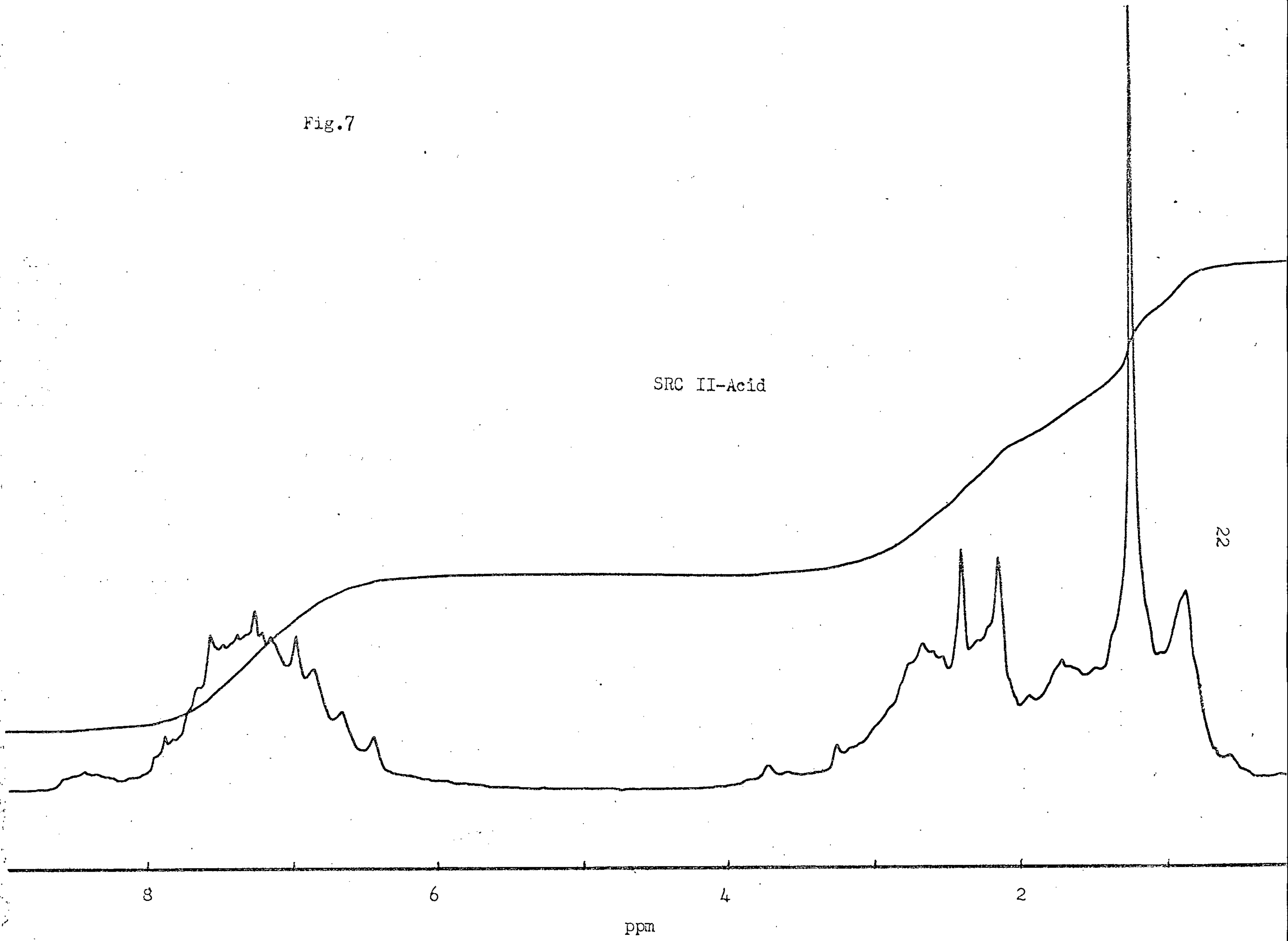


Fig.8

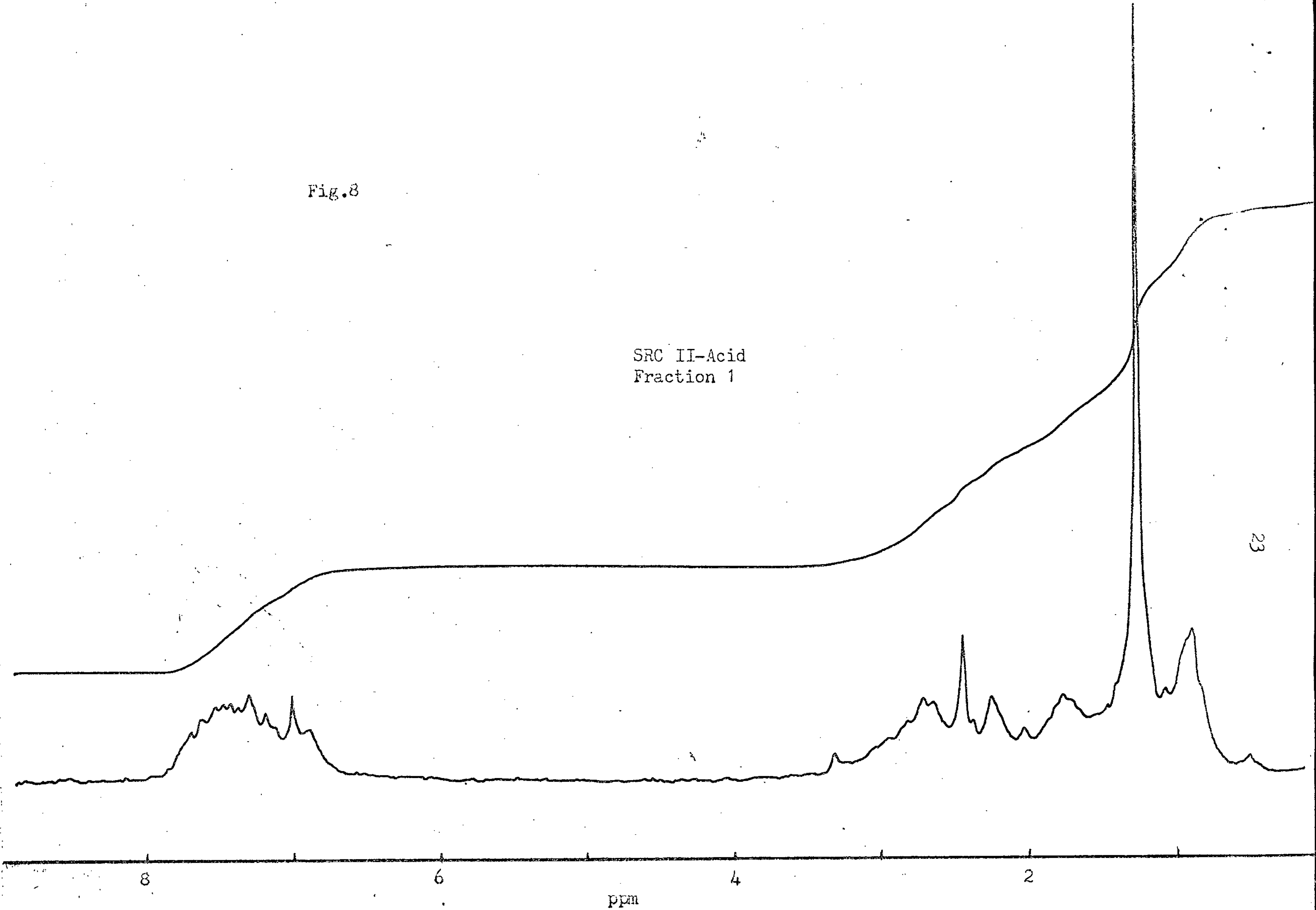


Fig.9

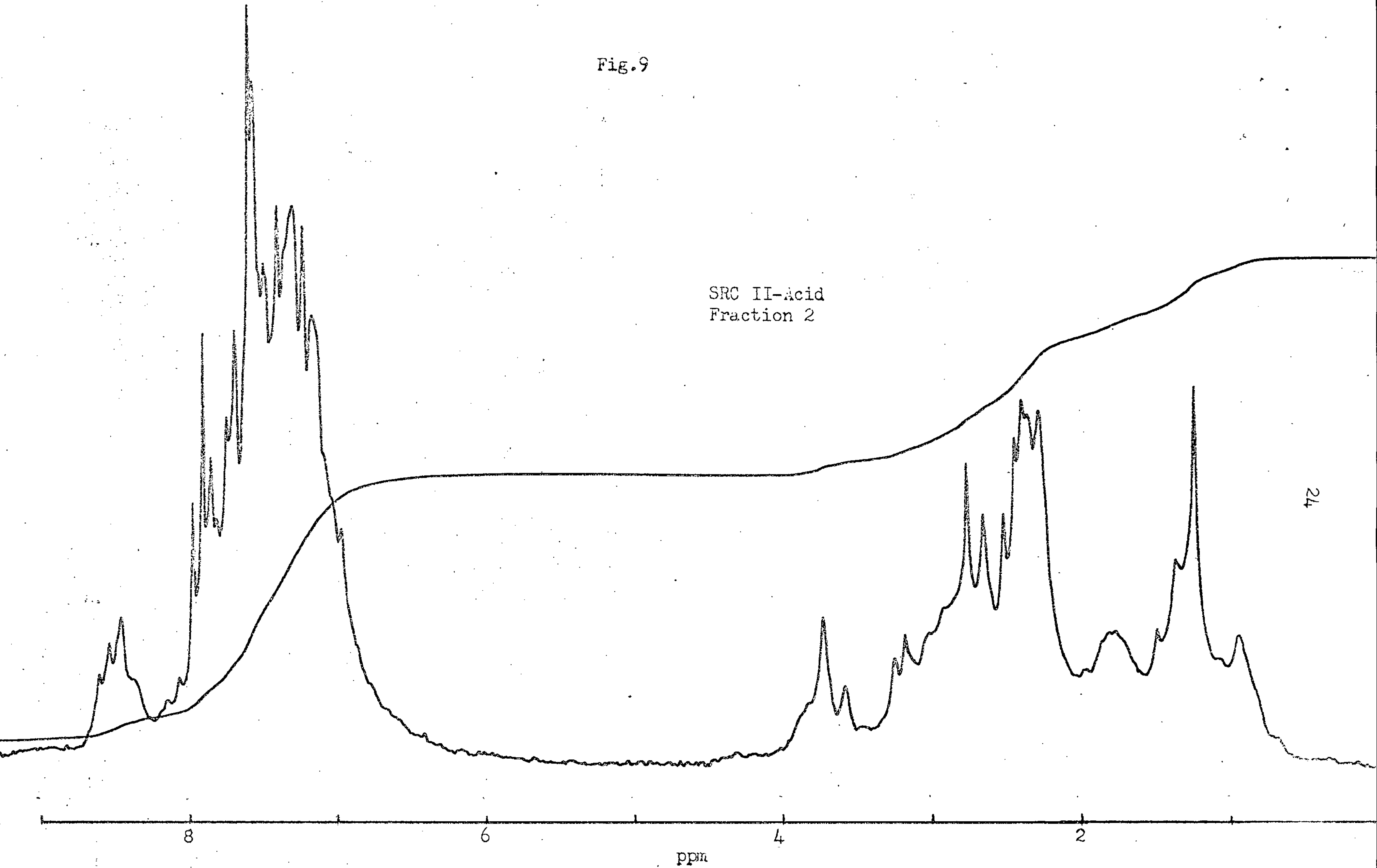


Fig.10

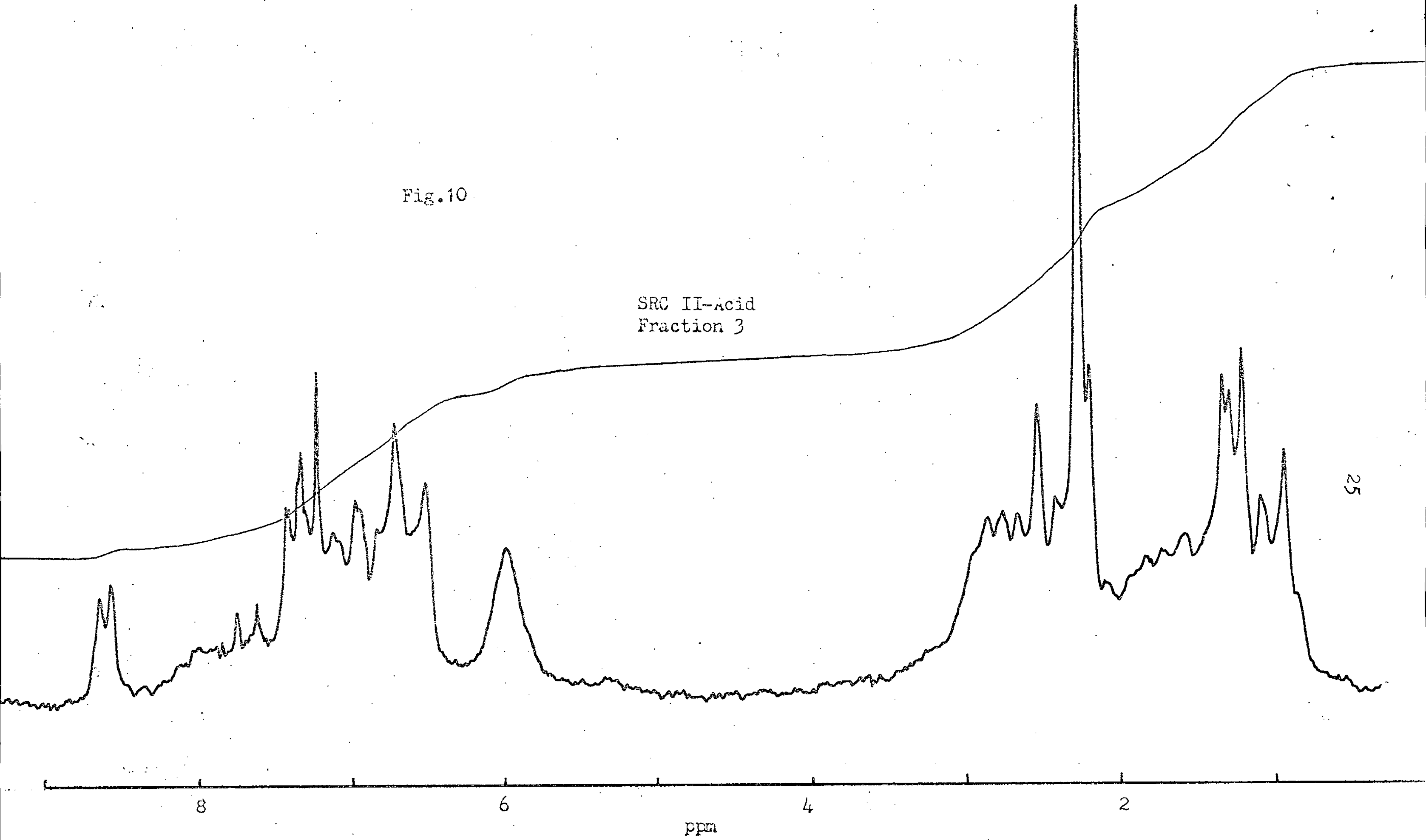


Fig.11

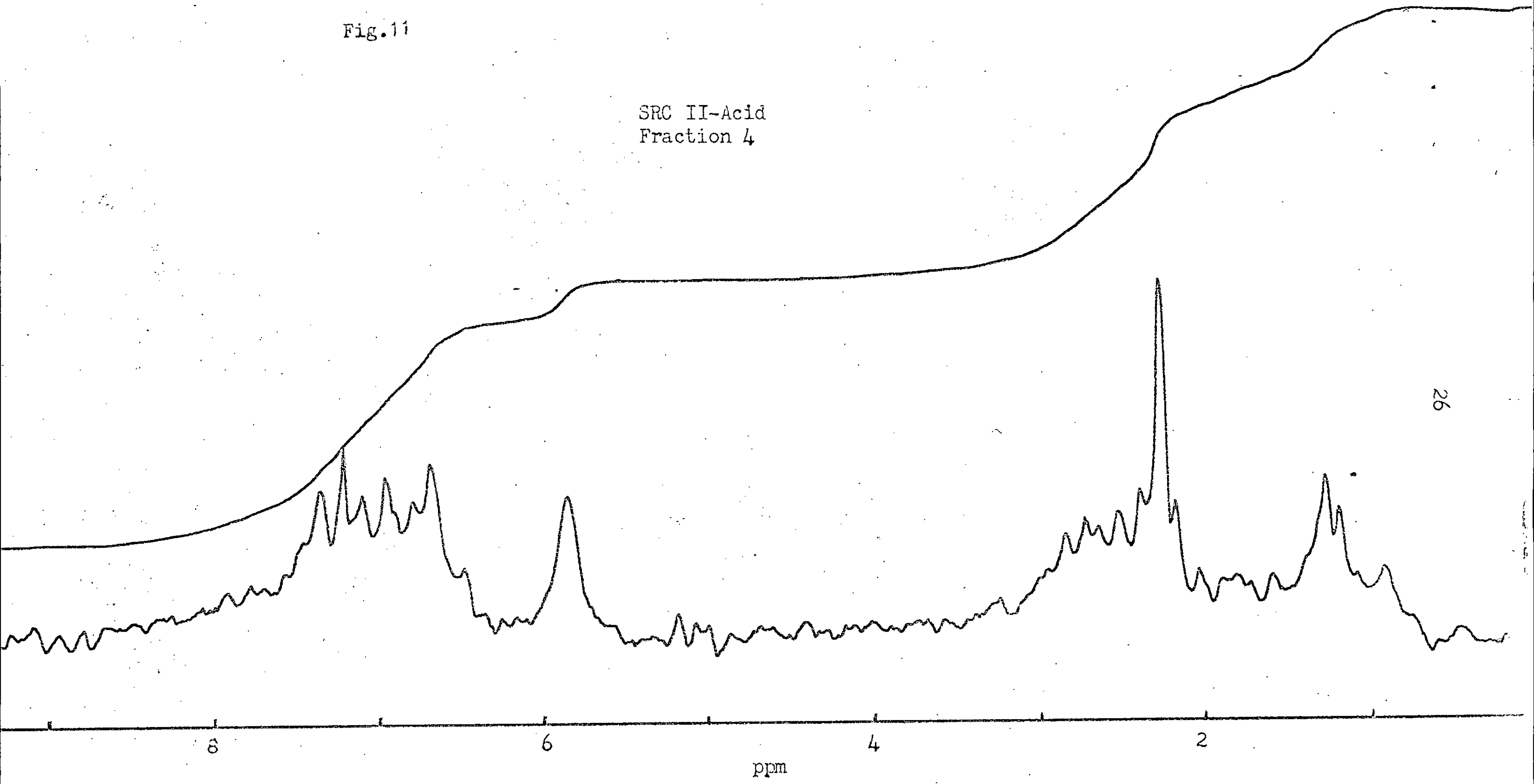
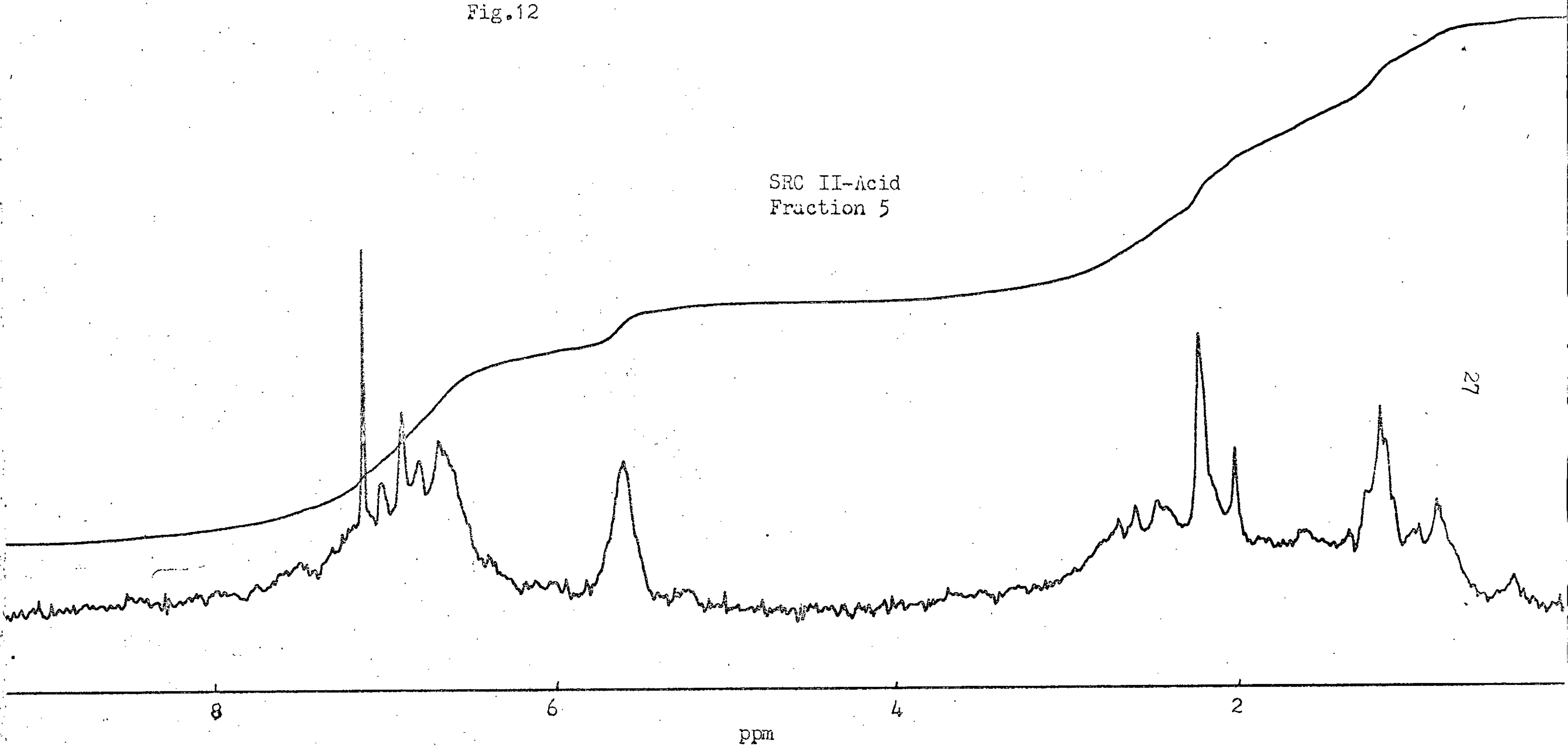


Fig.12



Personnel

The Principal Investigator devoted 1/3 time, during January - March 1979, to the work of this contract. Dr. K. C. Tewari and Dr. T. Hara devoted 40 hours/week in this period. The following students have participated: Lilly Young, Dan Croitora and David Susco.