

VISCOSITY OF COAL LIQUIDS - THE EFFECT OF CHARACTER  
AND CONTENT OF THE NON-DISTILLABLE PORTION

by

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ABSTRACT

In coal liquefaction by direct hydrogenation, the objective of processes under study is to produce a liquid which might substitute for petroleum in fuel and refining applications. One difficulty with such coal liquids is the high viscosity exhibited by these materials at ambient temperature. This is especially important if the product were not to be fractionated by distillation but rather be filtered or centrifuged and transported by pipeline to be used directly as a boiler fuel. This report describes experimental work and conclusions concerning the effect of the heavy ends of coal liquids on the viscosity. In this work various distillation residues were dissolved in anthracene oil to produce a simulated coal liquid. The solvent was held constant for each of the residues studied; therefore, differences in the character of these distillation residues would cause the resulting solutions to be of varying viscosity. The character of the distillation residues was studied by high pressure liquid chromatography (HPLC) for molecular weight distribution, solubility in toluene and hexane, column chromatography, nonaqueous titration for weak acids and bases, elemental analyses for nitrogen and oxygen, and mass spectrometry using a solids probe inlet. Of these properties determined for the various solid residues, almost all were found to correlate with viscosity of the solutions. Molecular weight, oxygen content, concentration of weak acids, and hexane soluble constituents were most notable in correlating with solution viscosity. The mass spectral data, concentration of weak bases, and concentration of asphaltenes did not correlate with viscosity. It appears that hydrogen bonding is more important in defining the effect of asphaltenes and pre-asphaltenes on viscosity than are acid-base salt formation interactions. Of interest is the fact that in liquids where pre-asphaltenes are major constituents, the effect of asphaltene content is overridden. Pre-asphaltenes have a greater effect on increasing viscosity than do comparable concentrations of asphaltenes in coal liquids.

This work helps to define the problem to be overcome in producing low viscosity oil from coal without distillation of product. It appears to be absolutely critical to minimize the concentration of non-distillable materials in coal liquids as well as to reduce the molecular weight, acid content, and concentration of pre-asphaltenes in the oil. The effect of concentration of non-distillable material in a coal derived oil is dramatic; an increase from 20 pct non-distillable to 30 pct non-distillable for the oils studied increased the viscosity by a factor of approximately 30.

#### INTRODUCTION

At the Grand Forks Energy Research Center (GFERC) the CO-Steam process<sup>1</sup> for liquefaction of low-rank Western coals is being studied. This research was pioneered at the ERDA Pittsburgh Energy Research Center (PERC) where bench scale batch and continuous experiments were conducted. Work is in progress at GFERC to determine reaction kinetics, to evaluate process design, to optimize reactor configurations, and to characterize the liquid product in detail. One important result obtained thus far is that the molecular weight of the non-distillable portion of CO-Steam product is reduced rapidly at temperatures above 460° C. For these studies a one-liter batch autoclave is used and a 3-lb/hr continuous unit is under construction and will be operating in the near future. Product characterization is accomplished by a combination of analytical techniques including high resolution mass spectrometry, low voltage mass spectrometry<sup>2</sup> (LVMS), gas chromatography-mass spectrometry (GC/MS), high pressure liquid chromatography (HPLC) and column chromatography<sup>3</sup>.

In early product characterization work at GFERC, two CO-Steam product oils from PERC were encountered which had obviously different viscosities but essentially the same concentration of distillation residue (at 250° C and 1 torr). The volatile portions of the two liquids analyzed by LVMS and GC/MS showed the two distillates to be virtually identical as to the type and amount of the compounds present. It appeared that differences in viscosity of these two liquids was due to the character of the non-distillable portion. A program was then initiated to characterize properties of the distillation residue which might affect viscosity. The procedures to be described in the experimental section were applied to three distillation residues from coal liquefaction products (two CO-Steam liquids and a Synthoil liquid<sup>4</sup>) and to five solvent-refined coals<sup>5</sup> (SRC's) which resemble the distillation residues of CO-Steam liquefaction products.

The viscosity of coal liquids and petroleum heavy ends has been the subject of some investigation, and the effect of the asphaltene content has been shown to be important in previous studies.<sup>6-8</sup> Coal derived oils and petroleum oils which contained from 10 to 30 pct asphaltene showed a marked increase in viscosity with increasing concentrations of asphaltene. Removal of polar materials from a solid petroleum distillation residue gave saturate and aromatic fractions which were liquids.<sup>9</sup> A paper by Burk and Kutta<sup>10</sup> showed that molten asphaltenes exhibited a lower viscosity than do molten pre-asphaltenes at the same temperature. Solution viscosity of Athabasca asphaltene has been investigated by Moschopedis, et al.<sup>11</sup>

One explanation for the marked increase in viscosity caused by asphaltene materials has been suggested to be acid-base interactions.<sup>6</sup> Asphaltenes are polar compounds having hydroxyl, acidic nitrogen, and basic nitrogen groups. Possible acid-base interactions between hydroxyl or acidic nitrogen and basic nitrogen functions is thought to cause molecular aggregation. This would lead to very high resulting molecular weights and a corresponding trend toward highly viscous liquids. Data presented in this study, however, suggests that hydrogen bonding rather than acid-base interactions is responsible for the synergistic effect noted for asphaltene on viscosity. Because neither weak base content nor percent nitrogen correlate with viscosity, it appears that the content of weak base is not effective in defining molecular interactions among the asphaltene molecules.

## EXPERIMENTAL

### Materials Studied

The CO-Steam liquids and Synthoil liquid were obtained from the Pittsburgh Energy Research Center. Several grams of each liquid was distilled in a Kugelrohr oven at 250° C and 1 torr. The resulting distillation residue was removed and ground to minus 200 mesh for preparation of solutions. The solvent refined coals studied were obtained from Pittsburg and Midway Coal Mining Co., Southern Services Inc., and the University of North Dakota (Project Lignite). Simulated coal liquids were made by dissolving 25 wt pct of the distillation residues or SRC's in anthracene oil. This concentration allowed differences in viscosity caused by various properties of the dissolved solids to be apparent and measurable. The viscosities were measured using a Brookfield viscometer, and the temperature of the liquids was held at 25.00 + .03° C using a constant temperature bath while the viscosity was being measured. The solutions were prepared by warming and stirring a mixture of the powdered solid with anthracene oil for 16 hours. No undissolved solids were observed, and the log of viscosity was linear with concentration, showing that solution of the distillation residues or SRC's was complete.

### Analytical Methods Used to Characterize Residues

#### Molecular Weight

The molecular weight of the residues was determined by dissolving the sample to 1 wt pct in tetrahydrofuran. Approximately 90 pct or more of each solid was soluble in tetrahydrofuran, so the value measured represented the molecular weight of virtually all of the sample. The one percent solution was injected into a Waters high pressure liquid chromatograph using 1-500 Angstrom and 3-100 Angstrom microstyragel columns which had been previously calibrated using the polystyrene standard supplied by Waters to measure molecular weight in the range encountered. Data were recorded using a strip chart recorder, and values for average molecular weight in the molecular weight ranges obtained are illustrated in Figure 1.

### Content of Asphaltene and Pre-asphaltene

The distillation residues and SRC's were dissolved in a minimum quantity of tetrahydrofuran. Toluene was then added to produce a solution containing 95 pct toluene, thus precipitating the toluene-insoluble pre-asphaltenes. The toluene solution, containing the asphaltenes and oil, was filtered. The filtrate was then concentrated, and hexane was added to precipitate asphaltenes from a 95 pct hexane solution; asphaltenes were separated by filtration. The pre-asphaltene, asphaltene, and hexane soluble oil were measured by determining the weight of each fraction separated from the original solid.

Column chromatography using alumina and a gradient elution approach<sup>3</sup> was used to determine the concentration of hydrocarbons plus ethers contained in the distillation residue and SRC. The sample of solid to be analyzed was preadsorbed on neutral alumina and added to a column containing alumina. Toluene was passed through the column and the hydrocarbons plus ethers were collected. The toluene was evaporated and the weight of material eluted was measured. The content of hexane soluble oil, as well as hydrocarbon plus ether compounds in the sample, were found to correlate with viscosity. Data are summarized in Table 1 for the concentration of asphaltene, pre-asphaltene, hexane soluble oil, and non-polar compounds in the solids studied.

### Non-aqueous Titration for Acid and Bases

The solids to be analyzed for acids were weighed to give approximately 0.4 grams of the solid; this was then dissolved in 50 ml of pyridine and protected from atmospheric carbon dioxide using nitrogen. The sample was titrated with tetrabutyl ammonium hydroxide in methanol/benzene as solvent using a glass versus methanol modified calomel electrode system. Data were recorded using a strip chart recorder. Weak bases were determined in an analogous way except that the titrant was perchloric acid in dioxane and the titration medium was 9:1 tetrahydrofuran/acetic acid.

### Elemental Analysis

Nitrogen was determined using the Kjeldahl method and oxygen was measured by neutron activation analysis. The activation analysis was performed by Intelcom Rad. Tech., San Diego, CA.

### Mass Spectrometry of Residues

The solids to be analyzed by mass spectrometry were placed in weighed one millimeter sample tubes and introduced into the solids probe inlet of a DuPont 21-491B low resolution mass spectrometer. The solids probe was heated to 200° and a mass spectrum of the vaporized material was obtained. After heating for several minutes at 200° no further vaporization of samples was evidenced by the absence of peaks in the mass spectrum. The capillary tube was removed and weighed to determine the quantity of material vaporized.

After weighing, the capillary tube was put back into the mass spectrometer and heated to 350° where another spectrum of the volatile material was recorded. After 350° heating for several minutes (to the point where no further sample vaporized) the capillary tube was removed from the mass spectrometer inlet and weighed to determine the total quantity of material vaporized. Approximately 1 milligram samples were used, and a Cahn Model 4700 electrobalance was employed for determining weight changes.

## RESULTS AND DISCUSSION

### Effective Concentration of Residue

The change in viscosity with concentration of residue in the simulated coal liquids is most dramatic for three different residues dissolved in anthracene oil in the range of 20-30 pct concentration. Figure 2 shows that the viscosity of the resulting solution can be increased by a factor of 20-40 for a 50 pct (relative) change in concentration of residue. Reducing the concentration of residue is perhaps the most important property to be influenced by changes in process variables. To make a product with a low concentration of residue is a first objective, and then liquefaction conditions might be changed so as to give non-distillable material which will minimize viscosity of the resulting coal liquid.

### Properties of Residues Which Correlate with Viscosity

The relationship between non-polar content and log viscosity is illustrated in figure 3. Both the percent soluble in hexane and the saturates plus aromatics obtained by elution in the column chromatography is shown to be a linear plot with a negative slope, indicating that the greater the concentration of hexane soluble material in the distillation residue, the lower will be the viscosity. Inversely, figure 4 shows a plot of pre-asphaltene content and percent of polar and polymeric material versus log viscosity. Again a reasonable correlation is seen. The asphaltene content related to viscosity shows somewhat random distribution. This is true because all of the residues studied have a significant content of pre-asphaltenes, and the effect of the asphaltenes is somewhat overridden by this large concentration of more effective viscosity-increasing constituents.

Data obtained previously by Sternberg et al<sup>4</sup> for variations of viscosity of Synthoil products with asphaltene content can be explained in terms of these results. When their data is replotted as log of viscosity versus percent asphaltene, the relationship is linear in the range of 5-20 pct asphaltenes; however, Synthoil liquids having from 20-40 pct asphaltenes show a positive deviation from linearity with log viscosity versus percent asphaltene. This positive deviation illustrates the effect of the pre-asphaltenes in those Synthoil liquids having high asphaltene content. Those materials with high asphaltene would have correspondingly more pre-asphaltene, and it is more effective in raising viscosity than is asphaltene.

The correlation of molecular weight with log viscosity is also linear and is illustrated in figure 5. When the average molecular weight of the distillation residues varied over the range of 290 to 500, the resulting solution's viscosity changed by a factor of 15. The material of molecular weight greater than 750 in the molecular weight distributions (Figure 1) may be the most important contributor to the increase in viscosity. These high molecular weight species in particular could lead to pronounced viscosity increases as was noted for pre-asphaltenes.

Examination of the distillation residues and SRC's directly by mass spectrometry did not yield very useful data. Only 10 to 25 pct of the SRC or residue was volatile in the mass spectrometer inlet, and no clear correlation could be drawn.

The variation of viscosity with both oxygen content and weak acid content is illustrated in figure 6. Molecular weight, weak acid content, and oxygen content of the non-distillable portion of coal liquids are all reduced by more severe reaction conditions, and this brings about an accompanying decrease in viscosity. It is not clear which of these properties are most important in defining the viscosity of the resulting liquid. Both molecular weight and concentration of polar groups could be important, and at this time, the data does not show which of these two parameters is predominant.

Of particular note, however, is that the weak base content and the percent nitrogen does not correlate with viscosity. Thus, the suggestion that acid-base interactions are responsible for highly viscous solutions of asphaltenes does not appear to be supported by this data. If both weak acids and weak bases were important, then viscosity should increase with the concentration of both. However, only acids appear to be definitive in establishing the viscosity. The conclusion which may be drawn is that hydrogen bonding of the hydroxyl groups and acidic nitrogen groups is of major importance while acid-base interactions are of lesser importance.

The various properties that have been shown to correlate directly with log viscosity are molecular weight, oxygen content, content of pre-asphaltene, and weak acid content. An inverse correlation is seen with the hexane solubility and saturates plus aromatics in the distillation residue. In a coal liquefaction process, all of these parameters will change in the direction of a lower viscosity product in a somewhat simultaneous way. It is not known at this point if one of these properties of the heavy ends would be more advantageously reduced during coal liquefaction than any of the other parameters studied. It can be safely stated, however, that decreasing the concentration of the non-distillable material in the coal liquid is absolutely necessary in lowering the viscosity of the product. Concurrent with this, improvement of the properties of this distillation residue tends to occur automatically. Further work is needed to define the changes in process variables which might bring about a reduction in undesirable properties of the distillation residue.

#### ACKNOWLEDGMENT

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TABLE 1. - Viscosity, molecular weight, and solubility

	Solution viscosity <sup>c/</sup> (centipoises)	Wt. Avg. molecular weight HPLC	Weight percent		
			Hexane solubles	Asphaltenes	Preasphaltenes
Synthoil residue.....	400	340	50.3	26.5	23.2
SRC 115.....	560	295	51.7	24.0	24.3
CO-Steam I residue <sup>a/</sup> ...	1552	450	24.2	12.3	63.5
CO-Steam II residue <sup>b/</sup> ...	1667	395	31.8	28.1	40.1
SRC Pitt 8....	1774	420	26.2	20.6	53.2
SRL M5C.....	1945	415	24.6	7.8	70.5
SRC 308.....	4467	495	15.6	14.4	70.0
SRC 122.....	6223	550	20.9	14.6	64.5

a/ Tubular reactor.

b/ Stirred autoclave.

c/ Viscosity of 25 pct (w/w) solution in anthracene oil at 25° C.

TABLE 2. - Column chromatographic separation

	Weight percent per fraction				
	Toluene 1	Chloroform(1) 2	Chloroform(2) 3	THF ethanol 4	Uneluted 5
Synthoil residue.....	15.9	1.7	37.6	40.0	4.8
SRC 115R.....	30.9	4.5	30.3	31.9	2.4
CO-Steam I residue <sup>a/</sup> ...	14.0	4.0	9.8	36.7	35.5
CO-Steam II residue <sup>b/</sup> ...	19.2	2.8	19.9	51.3	6.8
SRC Pitt 8....	13.5	3.8	14.7	63.2	4.8
SRL M5C.....	13.4	1.6	4.1	41.4	39.5
SRC 308.....	8.1	1.7	16.7	48.1	25.4
SRC 122.....	9.1	2.0	14.4	54.3	20.2

<sup>a/</sup> Tubular reactor.

<sup>b/</sup> Stirred autoclave.

TABLE 3. - Acid and base content

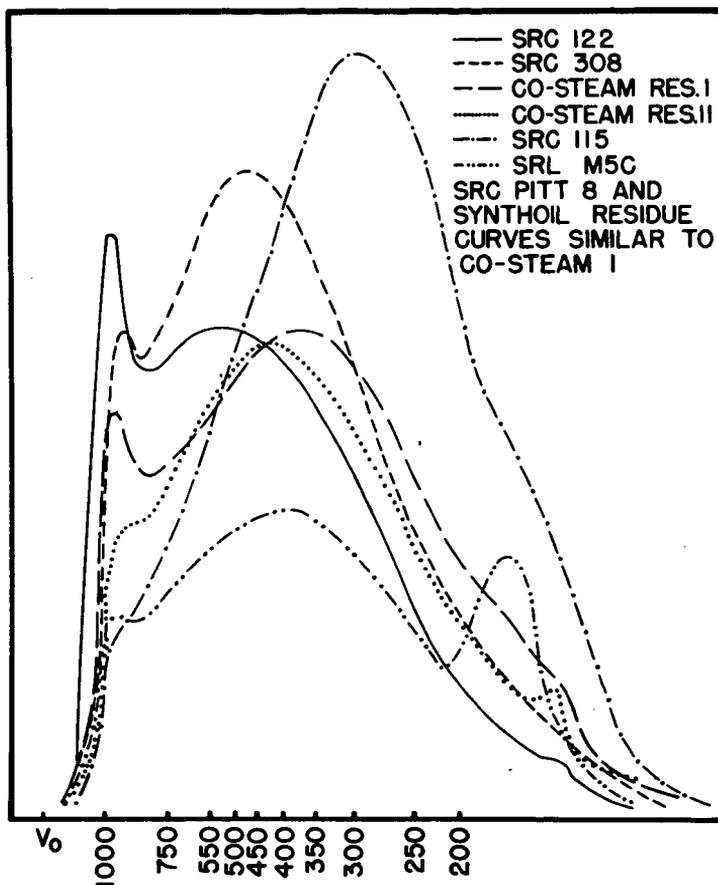
	Acidity meg H <sup>+</sup> /g	Pct oxygen, neutron activation	Basicity meg OH <sup>-</sup> /g	Pct N, Kjeldahl
Synthoil residue.....	2.066	---	0.750	---
SRC 115.....	1.481	1.55	0.711	1.70
CO-Steam I residue <sup>a/</sup> .....	1.661	7.03 <sup>c/</sup>	0.449	1.15
CO-Steam II residue <sup>b/</sup> .....	1.938	3.72	0.476	1.23
SRC Pitt 8.....	2.019	3.56	0.647	---
SRL M5C.....	2.060	---	0.522	---
SRC 308.....	2.285	4.32	0.786	1.78
SRC 122.....	2.531	4.69	0.713	1.55

a/ Tubular reactor.

b/ Stirred autoclave.

c/ Contains ash, inorganic oxygen present.

FIGURE I



MOLECULAR WEIGHT

MOLECULAR WEIGHT DISTRIBUTIONS OF SRC'S  
AND RESIDUES BY GEL PERMEATION HIGH  
PRESSURE LIQUID CHROMATOGRAPHY

FIGURE 2

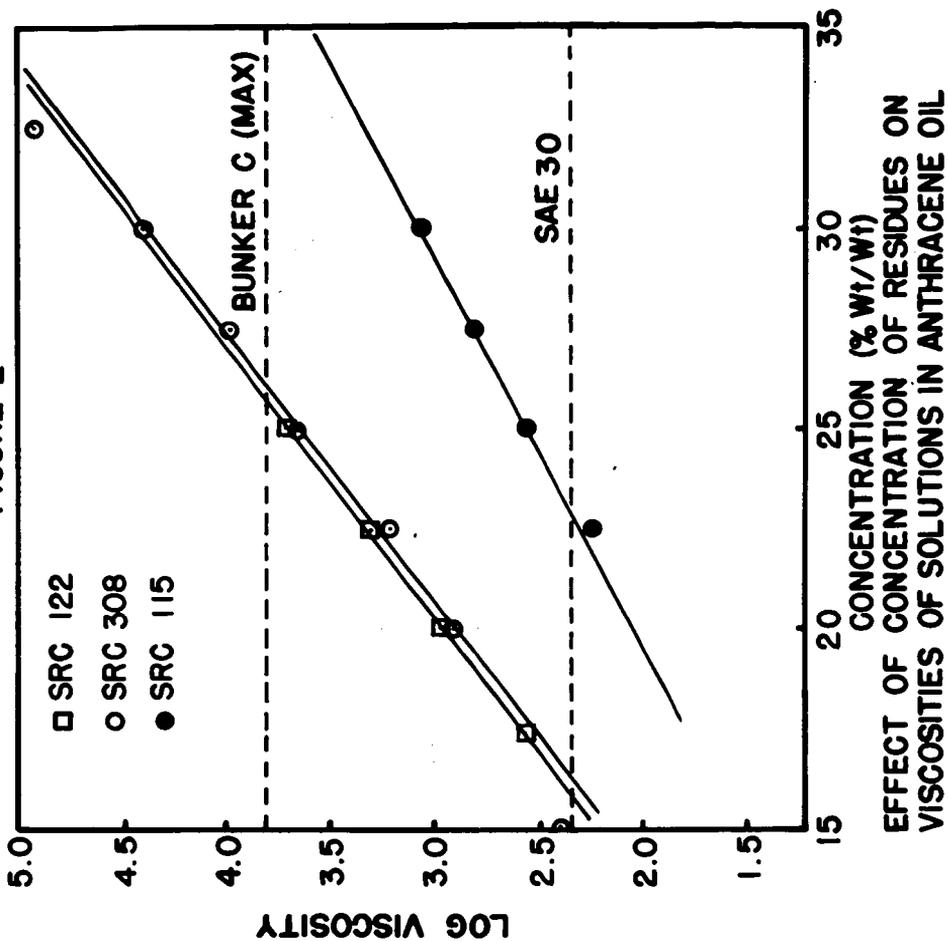
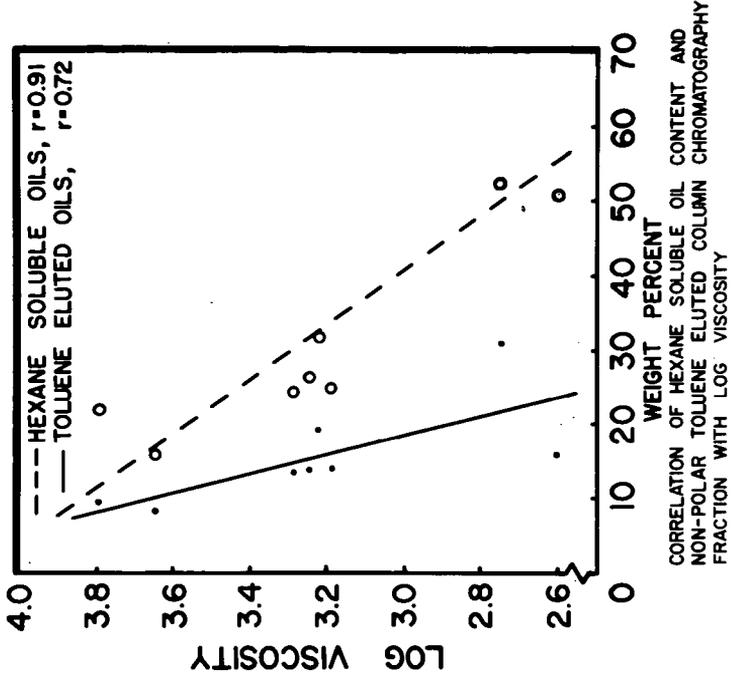


FIGURE 3



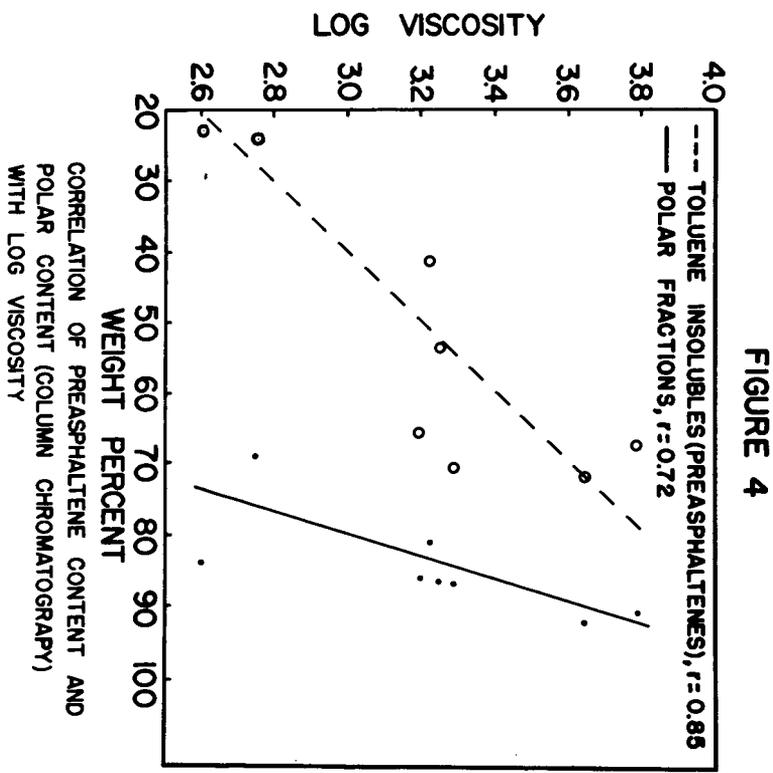


FIGURE 5

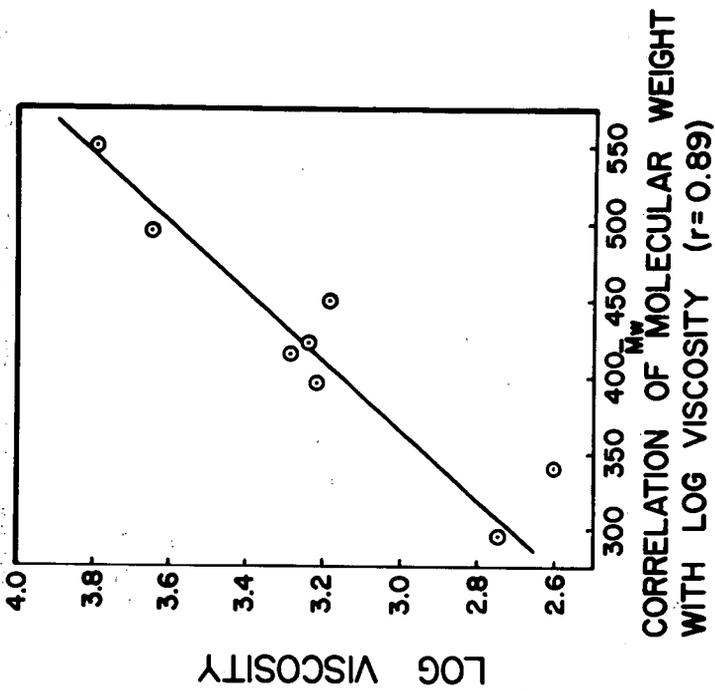


FIGURE 6

