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THE MOLECULAR WEIGHT DISTRIBUTION  
OF ATHABASCA BITUMEN

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ENERGY RESEARCH PROGRAM  
ENERGY RESEARCH LABORATORIES  
DIVISION REPORT ERP/ERL 83 - 59 (J)

ERP/ERL 83-59(J)

# THE MOLECULAR WEIGHT DISTRIBUTION OF ATHABASCA BITUMEN

by

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## INTRODUCTION

Catalytic hydrocracking studies in our laboratories (1-3) have indicated that the conversion of Athabasca bitumen is limited by diffusion in the catalyst pores. Since the dimensions of the diffusing species govern the optimum size of the catalyst pores, information on the molecular weight distribution of the bitumen was sought. For example, Hall and Herron (4) have shown that the molecules in the maltene fraction of a petroleum resid were small enough to enter the pores of a conventional catalyst whereas the molecules in the asphaltene fraction were too large.

The average molecular weight (AMW) of Athabasca bitumen asphaltenes has been reported by a number of workers. Sawatzky and Montgomery (5) found an AMW of 6110 using chemical methods. Initially Speight (6) examined two asphaltene fractions and reported AMW varying from 1380 to 6430. Subsequently, Speight et al(7) used the vapour press osmometry (VPO) technique with benzene, dibromomethane, pyridene and nitrobenzene solvents, and reported AMW values of 4850, 3430, 2655 and 2050 respectively. When a freezing point depression (FPD) technique (8) was used, they reported values of 8120-10910, 1780-3455, and 885-1360 with benzene, 2-methylenaphthalene and nitrobenzene solvents respectively. Ignasiak et al(9) used VPO with benzene, dibromomethane and pyridine solvents and reported AMW of 5920, 5480 and 5450. They subsequently (10) analyzed five asphaltene fractions prepared by gel permeation chromatography (GPC) and found AMW using a benzene as a solvent to vary from 1200-17,000. Suzuki et al(11) used benzene as a solvent and reported an AMW of 2750. Arguments favoring the lower molecular weight values have been presented (12) on the basis of depolymerization experiments (13).

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In the work reported here, the whole bitumen was used rather than just the high molecular weight asphaltene fraction, for two reasons. First, the character of the asphaltene fraction is known to be affected both by the solvent used for separation (14) and by the sequence in which solvents are used (15). Second, the whole bitumen is the feedstock for most conversion processes. However, catalysts designed for high conversions must be able to accommodate the largest molecules and not just molecules of average size.

### EXPERIMENTAL

Preparative scale separations were made using a Pye-Unicam LC-20 HPLC (high performance liquid chromatograph) adapted to take a 122 cm x 20 mm column packed with Styrogel 500 Å. Samples were injected onto the preparative column as a 1:2 mixture by weight of bitumen in THF (tetrahydrofuran). The flow rate of solvent (toluene) from the column was 9.75 ml per minute and fractions were collected over two minute intervals. Twenty fractionations were made, each time using a 1.5 mL sample composed of 32.1 m% bitumen in THF.

The solvent was removed under vacuum using a rotary evaporator. Only fractions 10 to 25 contained hydrocarbon material after the THF and toluene were removed. The molecular weight of each fraction was measured by three techniques; Vapour Pressure Osmometry (VPO) in THF, VPO in Benzene saturated with water, and by freezing point depression (FPD) in Benzene saturated with water (this solvent mixture will be referred to as benzene throughout this paper). Solutions of bitumen in THF were filtered through millipore filters before fractionation to remove ash and traces of insoluble organics (> 0.5%). The vapour pressure osmometer was a Model 301A VPO manufactured by Mechrolab Inc. The freezing point measurements were carried out on a Cryette A apparatus manufactured by Precision Systems Inc.

Analytical gel permeation chromatograms were obtained using a Water Associates ALC/GPC 244 equipped with refractive index and dual channel UV detectors and four µ-Styrogel columns, 10<sup>4</sup>, 10<sup>3</sup>, 500 and 100 Å. All analytical GPC's were run in HPLC grade THF at a flow rate of 1.50 ml per minute.

A Finnigan GC-MS system model 4000 with Incos Data System was used in the chemical ionization mode to analyze fractions 18, 19 and 20-25.

### RESULTS AND DISCUSSION

Four series of standard compounds of varying molecular weights were run on the analytical GPC and their refractive index (RI) retention volumes measured. The polystyrene compounds had molecular weights ranging from 600 to 35,000. The three long chain aliphatics and their molecular weights were tristearin (891.5), tripalmitin (807.3) and n-octodecane (254). The non-fused polynuclear aromatics were tetraphenylnaphtalene (432), tetraphenylcyclopentadienone (384), 1,2,3,4-tetraphenylcyclopentadiene (370), 1,1<sup>1</sup>-dinaphthyl (302), 4-benzylidiphenyl (244), and biphenyl (154). The fused polynuclear aromatics were tetraphenylporphin (614), rubicene (326), 3-methylcholanthrene (268), fluorene (166) and naphthalene (128).

As shown in Figure 1, the different families of compounds gave different calibrations when represented as the logarithm of the molecular weight versus retention volume. For the fused polynuclear aromatics there is considerable scatter and some "crossover", with lower molecular weight compounds being eluted before the higher molecular weight compounds. By comparing the calibration curve for long chain aliphatic compounds with that for fused polynuclear aromatic compounds, it is apparent that compounds having vastly different molecular weights can have the same retention time. Obviously the structure of the molecule as well as the molecular weight influences the retention volume. Similar<sup>at</sup> observations (16) were made previously with respect to coal molecules. In the past, it was shown (17) that the GPC technique could produce a universal calibration curve for many different polymers. Unfortunately, studies with one asphaltene have shown that its calibration curve was different (18) than the calibration curve for polymers. The data in Figure 1 suggests that different asphaltenes having substantially different molecular structures would also have different calibration curves.

The larger molecules in bitumen are considered to consist of a nucleus of fused rings to which aliphatic side chains are attached (6,12,13). Processing bitumen by coking or hydrocracking will tend to remove aliphatic side chains so that the character<sup>of the</sup> molecules<sup>will</sup> become more like fused aromatics. If the molecular weight distributions of the bitumen feedstock and the processed product are to be compared, the change in molecular structure during processing must be taken into account. Figure 1 shows that the molecular weight distribution of the feedstock and the products cannot be compared accurately by GPC since the results are greatly affected by molecular structure.

The preparative scale Styrogel column was able to separate 1.5 ml of a solution containing 32.1% bitumen by mass in THF, without flooding the column. The first trace of bituminous material was found in fraction 10, and fractions 20-25 were collected as a single entity since each contained a very small amount of material. The total mass of bitumen injected in 20 runs was 9.64 g. The sum of the masses of the recovered fractions, shown in Table 1 was 9.49 g which represents greater than 98% recovery.

As referred to previously (7-13) molecular weight results are known to be influenced by solvent, solvent concentration and technique used. Recently Chung et al(19) have shown that the solution concentrations used by most workers are responsible for erroneous results. They developed a new procedure which requires solutions to be sufficiently dilute to be in "the rectilinear region". In the work reported here, the procedure of Chung et al(19) was followed.

The consistency of the average molecular weight measurements was demonstrated by using three techniques; the freezing point depression method (FPD) using benzene, VPO using benzene, VPO using tetrahydrofuran and for the three lowest molecular weight fractions, gas chromatography-mass spectrometry (GCMS). Reproducible results were only obtained with the benzene solvent when it was saturated with water. Considerable work was attempted using nitrobenzene as the solvent. Unfortunately it was very hygroscopic and there were considerable variations in readings which were attributed to humidity changes in the laboratory.

Calibration curves with n-octadecane as <sup>a</sup>standard proved to be linear up to a concentration of 0.08 M in benzene by VPO and FPD, and up to 0.03 M in THF by VPO as shown in Figure 2. All measurements were made within these concentration ranges and when benzene was used as solvent, measurements were made at two different concentrations.

The molecular weight results are shown in Table 2. Fraction 10 was insoluble in benzene and its molecular weight could only be determined by VPO in THF. The molecular weight of fraction 11 determined in THF was greater than in benzene. Perhaps some of the material which was soluble in THF was not soluble in benzene. There was good agreement between the three methods for fractions 12-17 (86% of total material). For fractions 18,19 and 20-25, measurements in THF showed a steady decrease in molecular weight while those in benzene showed an unexpected increase in molecular weights. These three samples were subjected to GC-MS analysis in the chemical ionization mode which verified that the measurements in THF were correct. It must be assumed that these fractions are quite polar and, in the non-polar solvent, are exhibiting some association or H-bonding resulting in an increase in the apparent average molecular weight.

The relatively good agreement in Table 1 shows that the procedure of Chung et al(19) is able to produce comparable results when using different solvents (benzene and THF) and when using different techniques (VPO, FPD and GCMS). This agreement provides confidence in the absolute values of the numbers reported.

The amount of hydrocarbon in each of the bitumen fractions, shown in Table 1, is plotted as the ordinate in Figure 3. The abscissa is the average of the molecular weight values shown in Table 2. The molecular weights obtained with benzene for fractions 18,19 and 20-25 were not included in the average molecular weight for the reasons discussed above. Figure 3 is indicative of the molecular weight distribution in Athabasca bitumen. In the upper curve, the cumulative mass percent is the total amount of material having a molecular weight up to the value shown. The graph suggests that 100 percent is approached asymptotically and that there is very little material having a molecular weight greater than 5000. The graph also shows that 50 percent of the bitumen has a molecular weight of 500 or less. It is known that 50 percent of the bitumen distills at 525°C or lower (20). Pure compounds which have boiling points near 525°C also have molecular weights near 500. Although separation by distillation and separation by GPC are not the same, the comparison provides some credibility for the molecular weight distribution in Figure 3. It suggests that the non-distillable portion of the bitumen (oils, resins, and asphaltenes combined) contains compounds with molecular weights ranging from 500 to approximately 7000. The median molecular weight would be slightly less than 2000, which is comparable to some of the smaller values reported for asphaltene molecular weights in Athabasca bitumen (7-13).

The data in Figure 3 are considered to be the correct molecular weight distribution for Athabasca bitumen. The method used, collecting fractions from repetitive GPC runs followed by several molecular weight determinations of each fraction, was time consuming. Less work would have been required if analytical GPC could have been used. This technique was examined in more detail, in spite of the data in Figure 1 which indicated that it would not produce useful results.

There are two criteria which must be satisfied, if analytical GPC is to be a viable technique. First the detector response must be proportional to the quantity of material flowing through it. The hydrocarbon fractions in Table 1 were dissolved in THF and 50 microliter aliquotes were run on the analytical GPC. The retention times were recorded and the peak heights from the RI and UV (313 nm) detectors were measured. In Figure 4 the detector responses are shown as a function of the concentration of the bitumen fraction in the THF solvent. The data are scattered about a straight line through the origin. The smallest variation in response factor was seen

for the RI detector. However fractions 18,19 and 20-25 (representing only 4% of total material) were not detected, indicating that their average relative indices are the same as the THF solvent. Response factors are defined as the necessary detector response for a datum point to lie on the straight in Figure 4 divided by the actual detector response shown in Figure 4. These response factors are listed in Table 3. The required corrections ~~are~~<sup>were</sup> usually less than 30 percent.

Perhaps the detector response is related to the structure of the molecules in the bitumen fraction, as well as the concentration, shown in Figure 4. In a different study, GPC was performed on light distillate fractions having different boiling ranges. In those determinations, the detector response was not proportional to the concentration but also varied with the boiling point range of the distillate fraction. This finding may also have been caused by the detector response being related to the structure of molecules.

The second criteria~~s~~<sup>s</sup> is that the retention time or retention volume determined by analytical GPC must be proportional to the molecular weight. The retention time obtained by analytical GPC for the bitumen fractions in Table 1 are shown in Figure 5. These lines are curved particularly for the lower molecular weight compounds which have longer retention times. Furthermore the RI curve in Figure 5 cannot be superimposed on any of the lines in Figure 1. The curvature of the lines in Figure 5 may be caused by variations in molecular structure from one fraction to the next. The curves in Figure 5 are valid for Athabasca bitumen. They probably cannot be used as calibration curves for any processed product or any other heavy petroleum. These other materials are probably ore mixtures of molecules which are structurally different than Athabasca bitumen.

In summary, there are two problems associated with the use of analytical GPC in determining molecular weight distributions. The ideal detector response should be proportional to the mass of hydrocarbon. Unfortunately Figure 4 suggests that the detector response is influenced by factors other than the hydrocarbon mass. Also ideal GPC columns should separate molecules on the basis of molecular size or weight. Figures 1 and 5 suggest that the retention time on the GPC columns may be affected by factors other than the molecular weight of the species. One of the other factors may be differences in chemical structure of molecules. On a positive note there is a correlation between detector response and quantity of hydrocarbon and there is a correlation between retention time and molecular weight. Unfortunately these correlations are not of a sufficiently general nature. They probably cannot be used for quantitative work, with a wide variety of feedstocks and products.

If high conversions are to be obtained when Athabasca bitumen is processed using a heterogeneous hydrocracking catalyst, the catalyst pore structure must be large enough to accommodate the largest species, not just species of average size. Earlier work (2) has shown that diffusional limitations are present in pores up to 30 nm in diameter. Suggestions in the literature indicate that the diffusing species may be aggregates of large molecules. Asphaltene molecules may form micelles (21). Alternatively it has been suggested (7) that each asphaltene molecule interacts with resin molecules rather than with other asphaltene molecules. Weinberg and Yen (22) have shown that asphaltenes form mesophase, or liquid crystals which can be seen with an optical microscope, at temperatures similar to that used for hydrocracking. Therefore hydrocracking processing conditions the diffusing species may be precursors for the formation of mesophase and therefore very much larger than either the molecules measured in this study or colloidal micelles which are aggregates of these molecules.



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TABLE 1

ATHABASCA BITUMEN MASS DISTRIBUTION FROM  
PREPARATIVE SCALE GEL PERMEATION CHROMATOGRAPHY

Fraction Number	m% Bitumen in Fraction
10	4.51
11	5.46
12	6.86
13	12.20
14	19.40
15	23.14
16	16.80
17	7.82
18	2.99
19	0.48
20-25	0.34
Total	100.00

TABLE 2

MOLECULAR WEIGHTS OF ATHABASCA BITUMEN FRACTIONS OBTAINED  
BY PREPARATIVE SCALE GEL PERMEATION CHROMATOGRAPHY

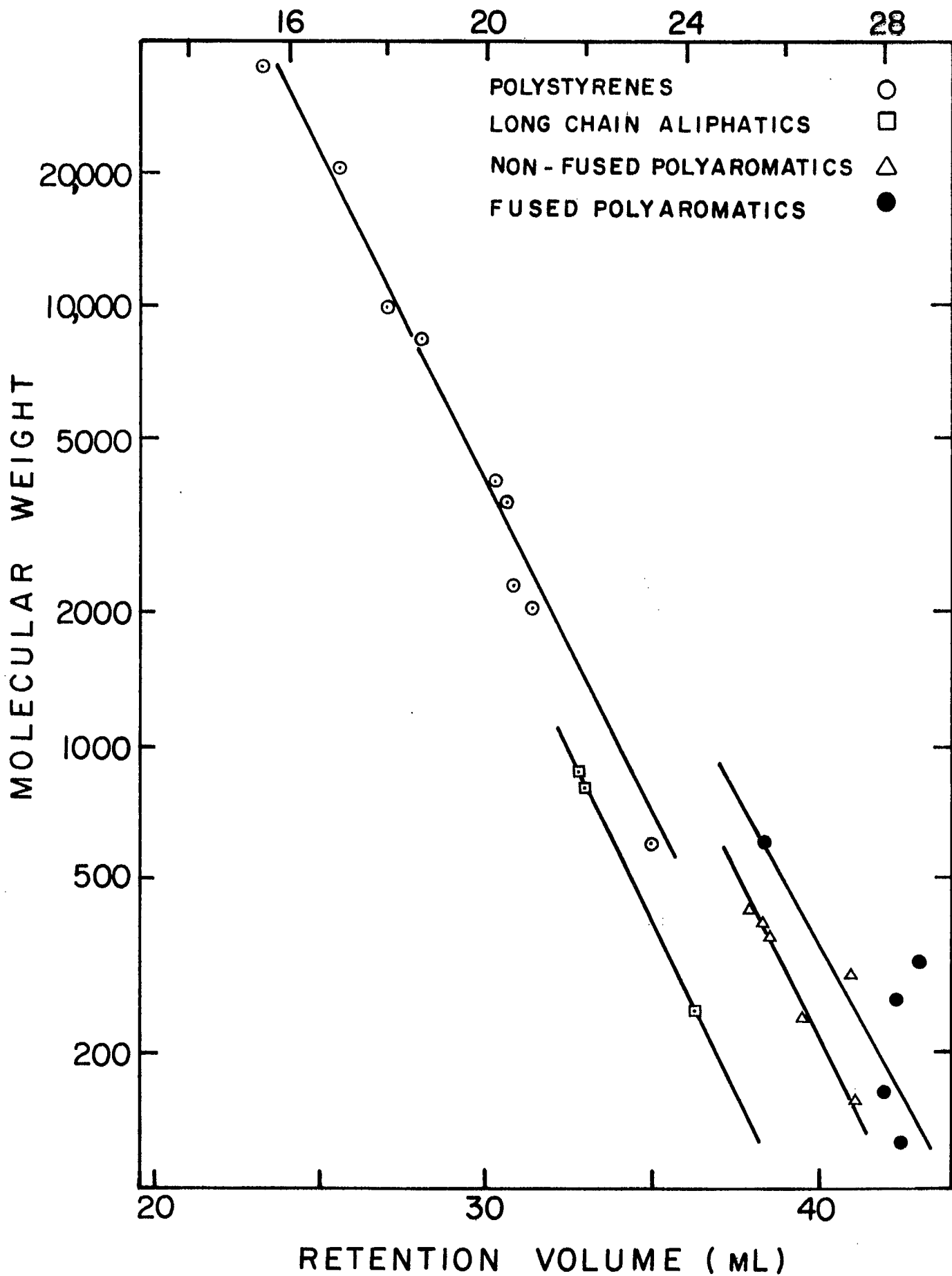
Fraction Number	MOLECULAR WEIGHTS BY VARIOUS METHODS			
	THF-VPO	B-VPO	B-FPD	GCMS
10	6688			
11	5468	3024	3293	
12	1680	1916	1892	
13	1423	1386	1372	
14	713	772	704	
15	504	476	434	
16	371	456	356	
17	368	414	376	
18	284	419	401	260
19	271	444	421	270
20-25	250	556	544	250

TABLE 3

## RESPONSE FACTORS FOR BITUMEN FRACTIONS

Fraction	U.V. Response Factor	R.I. Response Factor
10	1.16	1.37
11	0.97	0.97
12	0.82	0.78
13	0.87	0.92
14	1.03	0.96
15	1.31	1.09
16	1.03	1.02
17	0.90	1.07
18	0.68	∞
19	0.77	∞
20-25	5.25	∞

RETENTION TIME ( m )



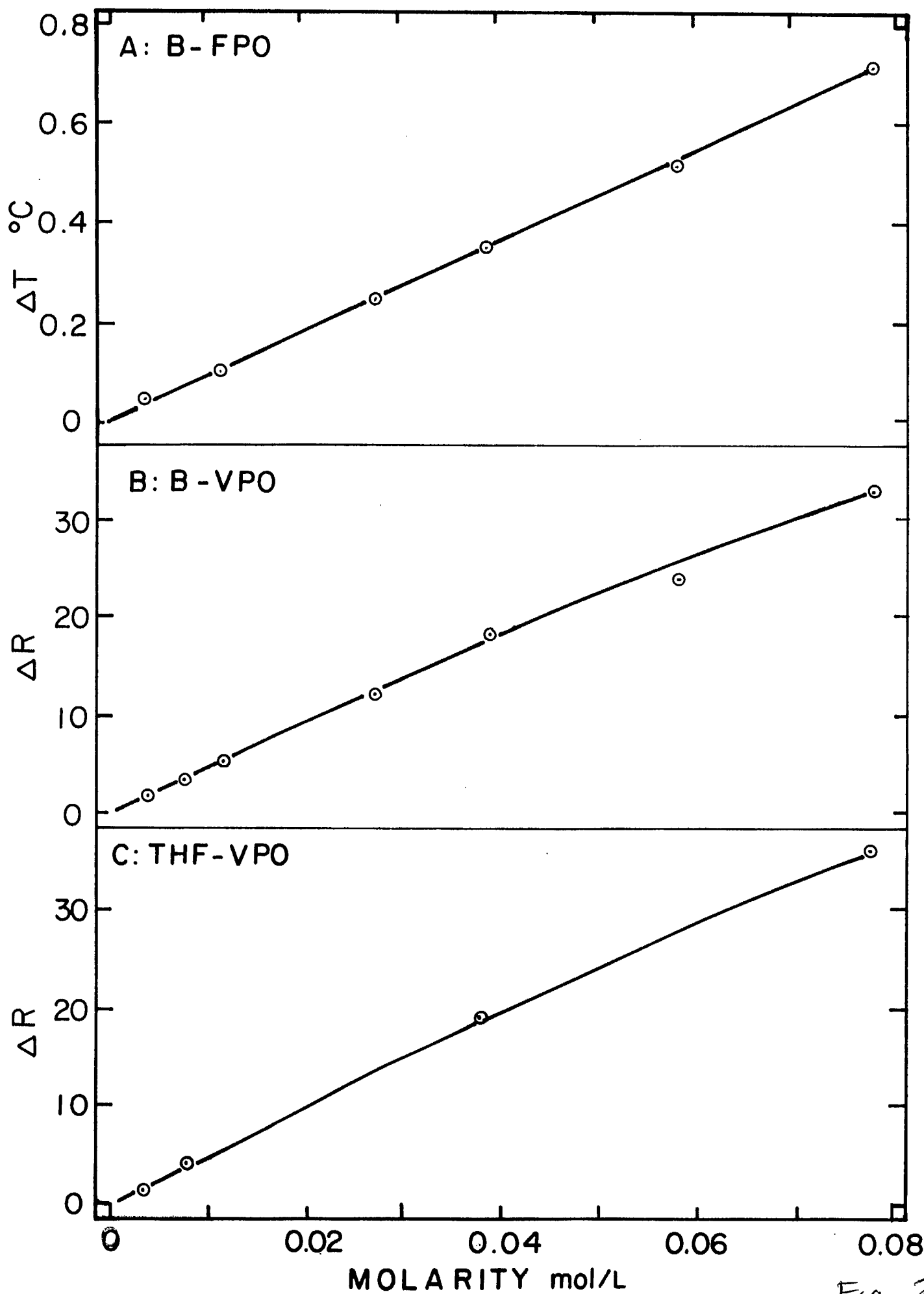
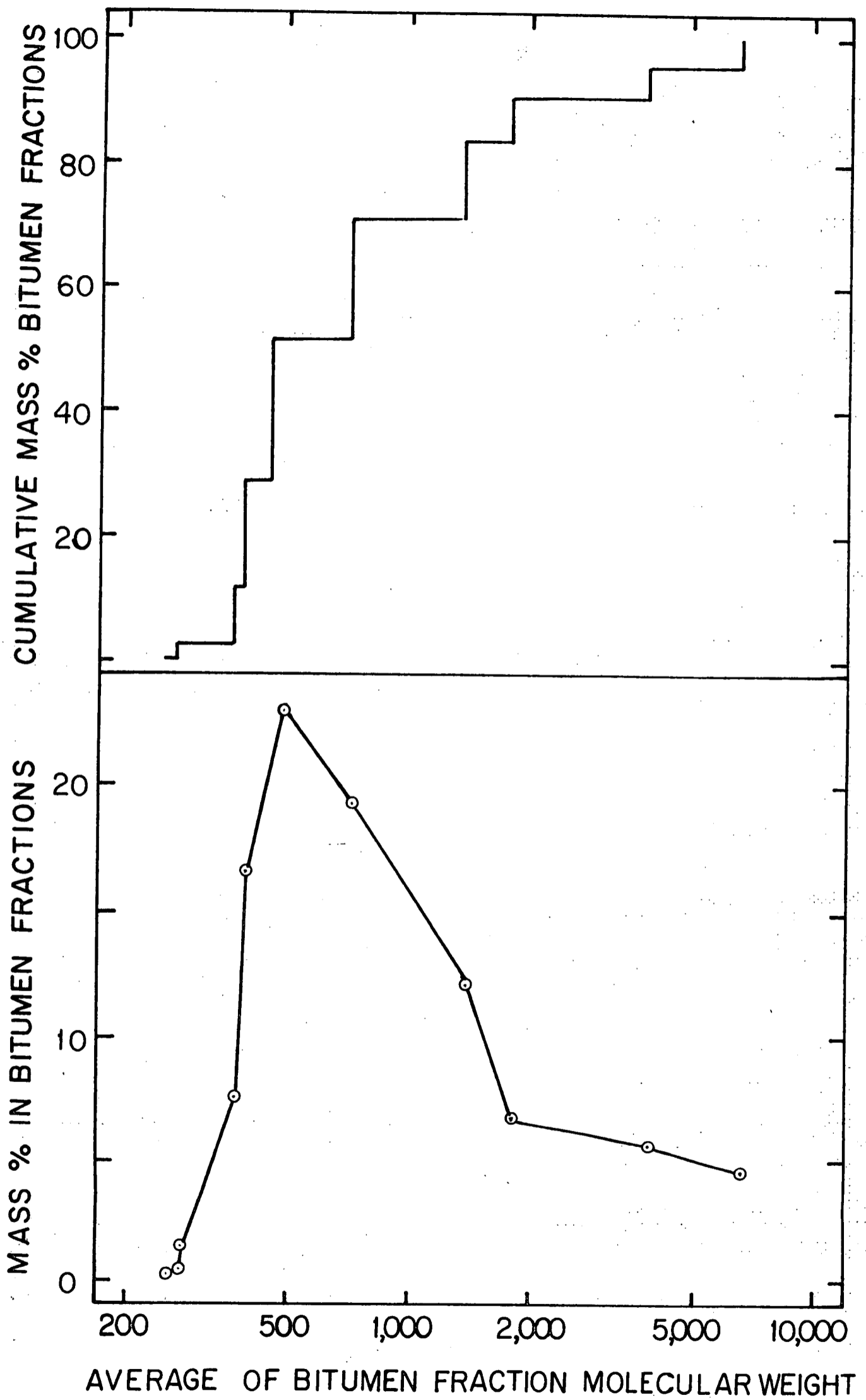


Fig 2



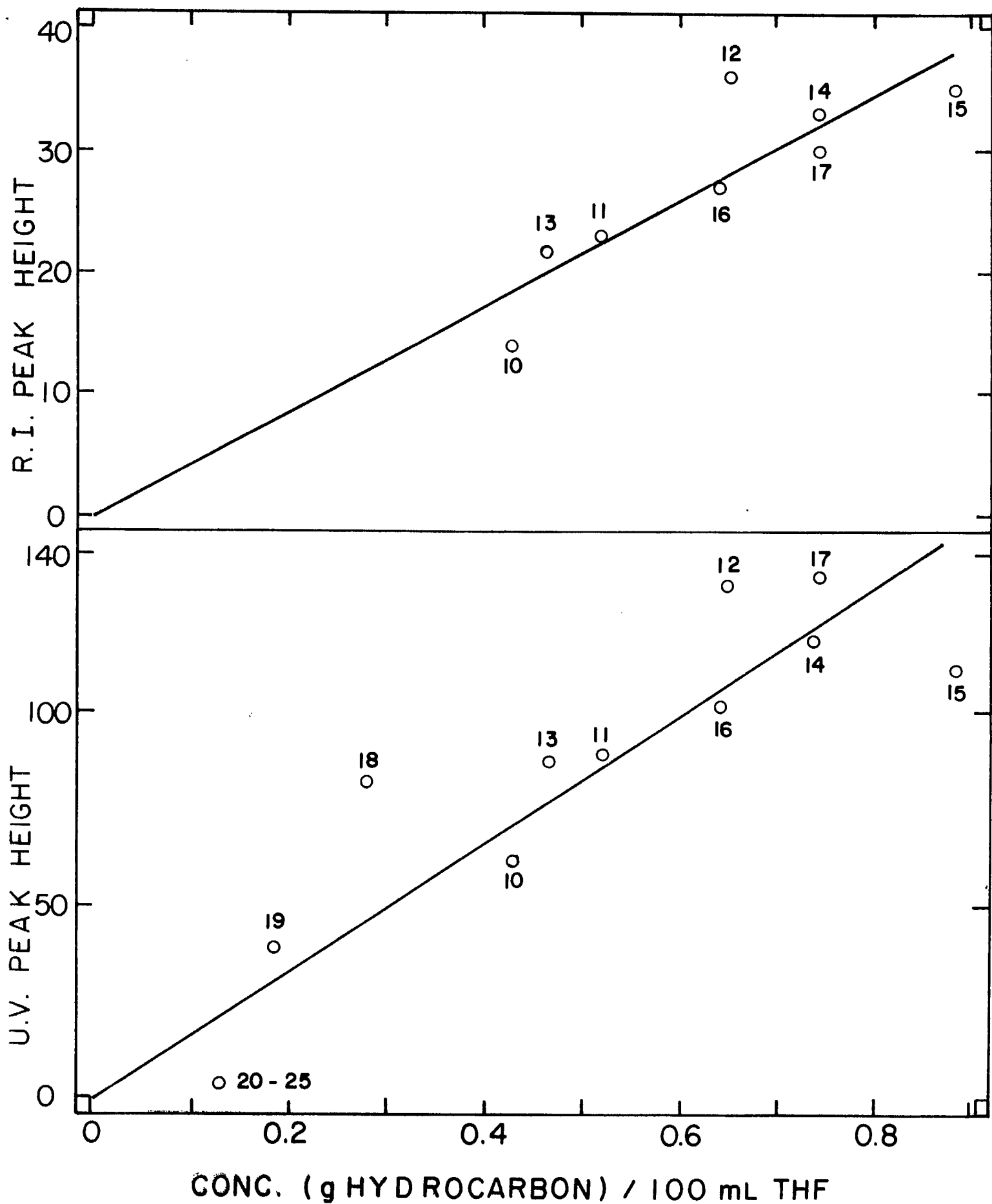


Fig 4



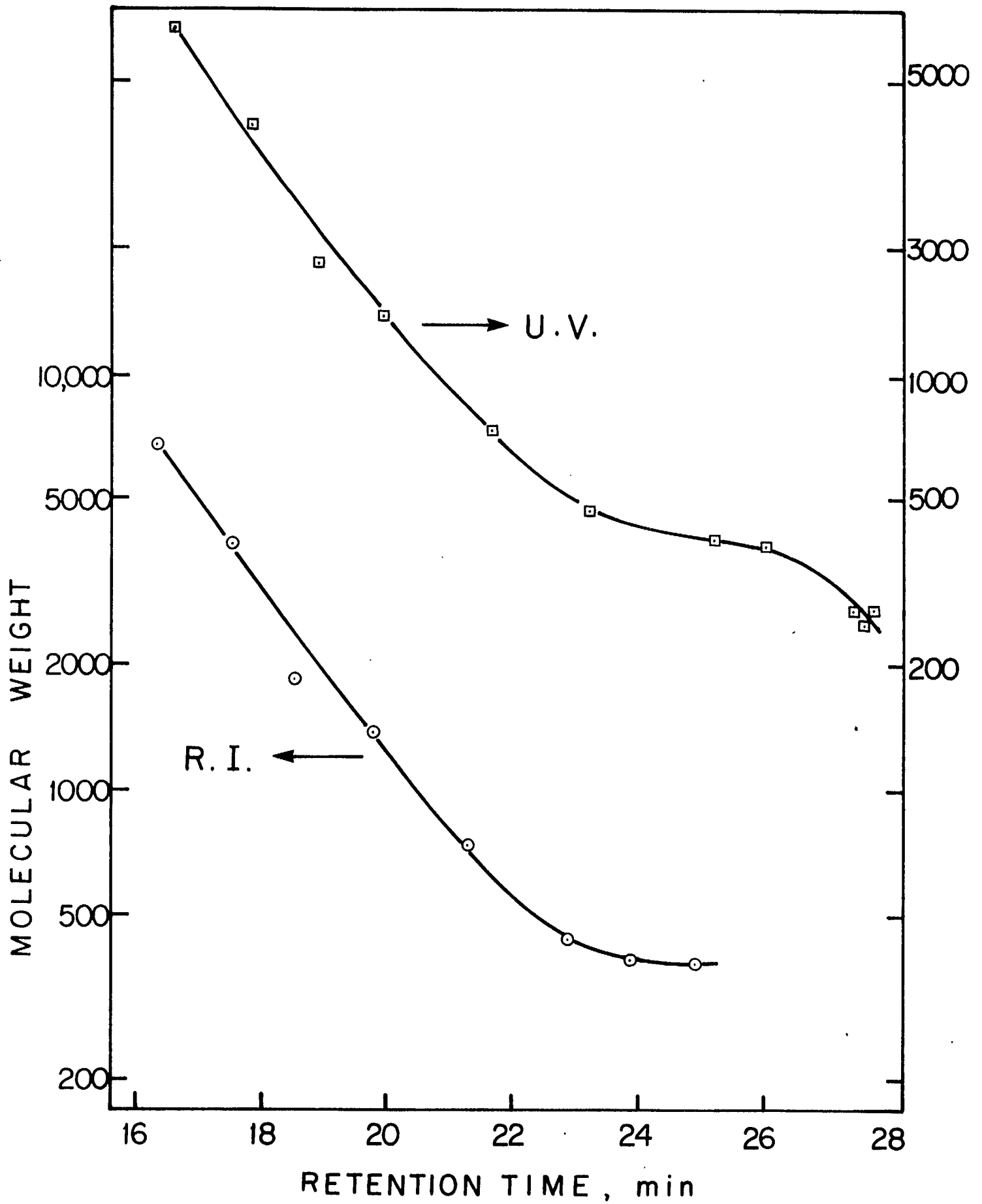


Fig 5

TEMPERATURE, °K

1000

500

333

250

log K

10

10

5

5

0

-5

-5

MoO<sub>3</sub> → MoS<sub>2</sub>

MoO<sub>2</sub> → MoS<sub>2</sub>

ZnO → ZnS

PbO → PbS

CoO

CuO → CuS

CaO → CaS

FeO → FeS

NiO → Ni<sub>3</sub>S<sub>2l</sub>

(Fe<sub>3</sub>O<sub>4</sub> → FeS)

(Fe<sub>2</sub>O<sub>3</sub> → FeS)

MgO

1.0

2.0

3.8

4.0

$\frac{1}{T} \times 1000, 1/^\circ K$

