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SYNTHESIS OF OLIGOMERIC MODELS OF COAL DERIVED MATERIALS FOR USE WITH GPC CALIBRATION

Quarterly Report for the Period October—December 1983

By
Richard J. Baltisberger
Martin B. Jones

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University of North Dakota
Grand Forks, North Dakota

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ABSTRACT

The purpose of the study was to develop a set of GPC calibration standards for asphaltene and preasphaltene analysis. A series of oligo(aryl ether) (1) and oligo(arylmethylenes) (2) from 170 to 580 g/mole were prepared via modified Ullmann-type reactions (ethers) and condensation of an aryl lithium derivative with an aryl carboxaldehyde, followed by reduction of the resulting carbonol (methylenes). These compounds were examined as

$$\underset{\underline{1}}{\left(Ar\text{-}O \right)_n} \qquad\qquad \underset{\underline{2}}{\left(ArCH_2 \right)_n}$$

molecular weight calibration standards for GPC analysis. A nearly linear plot was found to exist between the logarithm of molecular weight times mol fraction hydrogen versus retention volume with THF as the solvent (see Figure 6). Further this plot was coincident with commercial polystyrene standards (600-2000 g/mol) and with the majority of our lignite derived asphaltenes and preasphaltenes.

Work in our laboratory suggests that universal calibration plots for the gel permeation chromatographic (GPC) analysis of lignite derived preasphaltene and asphaltene liquefaction products are possible for determining number and weighted average molecular weight values. The data indicates that the acid content (OH mmol/g) and the hydrogen content (mole fraction or H/C mole ratio) are representative of the solubility parameters of the asphaltenes/preasphaltenes. Universal calibration plots based on the logarithm of the hydrodynamic volume, number average molecular weight times hydrogen content, result in a smooth curve coincident with polystyrene standards, model compounds, and lignite derived asphaltenes/preasphaltenes. The data which supports the above hypothesis is presently limited and has only been measured for lignite derived materials.

I. PURPOSE

One important facet of the characterization of coal derived materials is that of molecular weight determination. Number average molecular weight is usually obtained by vapor pressure osmometry measurements. However, no satisfactory method is available for determining weight average molecular weights. The latter values are useful in predicting rheological properties. Gel permeation chromatography (GPC) is a technique which should be most readily adaptable for this measurement. The other techniques of ultracentrifugation and light scattering are not as readily available as GPC. At this time, satisfactory GPC calibration standards which possess chemical structures similar to coal derived materials are non-existent.

The purpose of this study is to develop a useful set of GPC calibration standards for asphaltene and preaspaltene analyses. Our previous results suggest models in which coal derived preasphaltenes and asphaltenes are composed of oligomeric aromatic ethers of both diaryl and furan types. We plan to synthesize a series of model oligomers that are in agreement with the average structural formulas of some selected coal preasphaltenes as determined by pmr, elemental analyses and various oxygen derivatization procedures. These model compounds will be tested for use as calibration standards for both high pressure gel permeation chromatographic and vapor pressure osmometric procedures. Their response and retention times will be compared with coal preasphaltenes to determine the suitability of the model compounds as calibration standards.

II. OBJECTIVE AND SCOPE OF WORK

Task 1 Syntheses of Model Oligomers

Previous studies of the structure of asphaltenes and preasphaltenes suggest these coal derived materials are composed of a carbon skeleton composed of 2-4 ring aromatic centers connected by etheral or furan linkages. Model oligomers based on these types of structures will be synthesized in the molecular weight range of 300 to 800 g/mol. Oligomers will be synthesized with and without phenolic groups added to the structure.

Task 2 Vapor Pressure Osomometry

The molecular weights of the model oligomers will be measured by vapor pressure osmometric techniques. The model oligomers will be sent out for analysis by light scattering in order to compare the number average and weight average molecular weights. The number average molecular weight of several preasphaltene and asphaltene samples will be measured by vapor pressure osmometric techniques. Prior to analysis the samples will be separated into narrow molecular weight ranges by preparative column GPC techniques.

Task 3 Gel Permeation Chromatography

A series of model oligomers will be used to calibrate a high pressure gel permeation chromatographic column. Samples of the relatively narrow molecular weight ranges of preasphaltenes or asphaltenes will be tested on the column to determine if retention times are linear functions of the vapor pressure osmometric values. Several commercial packings, both high pressure and open column materials, will be tested.

III. PROGRESS TO DATE

Task 3 Gel Permeation Chromatography Testing

BACKGROUND

The application of GPC to the characterization of coal derived materials has been studied by a number of researchers (1-13). Coleman et al. (2-3) demonstrated that three column packings; styrene-divinylbenzene (Bio-Beads S-X4), cross-linked poly(acryloylmorpholine), and modified alkylated dextran (Sephadex LH-20) polymers; could be used for the GPC separation of THF and $CHCl_3$ solvent refined coal (SRC) fractions. Schwager et al. (1) isolated four SRC asphaltene fractions by preparative techniques using Bio-Beads SX8. A linear relationship between the logarithm of number average molecular weight and retention volume was observed using an analytical μ-styragel HPLC column. The analytical column was calibrated with a porphyrin, a series of aromatic hydrocarbons, and propylene glycols of known molecular weight. Curtis et al. (4) studied the characteristics of an SRC (Amax) using GPC techniques. The separation employed three μ-styragel columns using THF as the solvent and was calibrated with a series of polyethylene glycol and various polynuclear aromatic hydrocarbon standards. Sephadex LH-20 has also been used to fractionate the hexane soluble portion of the pyridine extract from a Sorachi coal (5). Khan (6) compared the use of GPC and vapor pressure osmometry (VPO) to obtain molecular weight data for the hexane soluble portion of three H-coal liquids. Two packings, polyvinylacetate (Fractogel PVC 500) and styrene-divinylbenzene copolymer (Topo Soda, G2000H10) were used as analytical columns. Calibration of the columns was accomplished by VPO measurement of number average molecular weight in toluene of preparative scale fractions obtained from a Fractogel column.

The above work has demonstrated that the quantitative interpretation of GPC chromatograms raises two problems. First, the response of the detector must remain constant on a per weight basis over the molecular range (i.e., type and distribution of chromophores must be constant). A constancy of uv absorbance per gram for a series of SRL materials has been reported in work by Ruud (9). This point needs to be investigated more thoroughly if weighted average molecular weights are to be calculated from GPC columns. A second problem, which is the focus of this research, is the establishment of the response curve with suitable calibration standards.

The establishment of a single calibration plot for the GPC analysis of coal derived materials appears to be at first glance a virtually impossible task because of the many series of homologous compounds each of which may have its own relationship of size, shape, and molecular weight with retention time. For example, rigid molecules like aromatics have smaller molecular volumes than do straight chain hydrocarbons of the same molecular weight (12). Anthony and Philip (12) have shown that hydrogen-bonding in THF as the chromatographic solvent leads to the formation of 1:1 adducts with such compounds as phenol, pyridine, or quinoline resulting in molecular sizes larger than a four membered aromatic ring hydrocarbon. Molecular shape and length are key factors in the GPC technique. A solution to the above problem is to use universal calibration plots. The intrinsic or limiting viscosity of the substance analyzed is included in the calibration plot where the logarithm of the product of limiting viscosity and molecular weight is plotted versus the retention time or volume. Brule (14) has shown that such an approach is satisfactory for the GPC analysis of petroleum asphaltenes using polystyrene standard oligomers. The advantage of a universal calibration plot is that the graph approaches a linear function of the hydrodynamic volume of the solute. The hydrodynamic volume is proportional to the product of molecular weight and the limiting solution (intrinsic) viscosity. Narrow molecular weight fractions should fall on the same curve regardless of polymer type. The disadvantage of the technique is that limiting viscosity must be measured for each eluent fraction during the separation. Our preliminary data suggest that the H/C ratio can be used in place of the limiting value. The limiting viscosity is a measurement of a series of viscosity values extrapolated to infinite dilution. The measurement of 3-5 viscosity values can be rather time consuming compared to the analysis of a H/C or mole fraction of hydrogen present in the sample.

Coal tars (15) and coal derived asphaltenes/preasphaltenes (1) behave as if they consist of members of different homologous series (similar types of compounds). Suuberg (15) studied the molecular weights of coal tars formed by flash pyrolysis of bituminous coals and found that these substances fit a linear plot of the logarithm of molecular weight versus retention times for the range 500 to 2500 g/mol. The tars did not follow the same linear plot as a series of polystyrene standards but were consistently eluted at larger volumes for the same molecular weight of polystyrene. This response would be exactly what one would expect for coal tars which contain polycondensed aromatics and few aliphatic groups as opposed to the benzene and aliphatic groups of polystyrene.

Schwager and Yen (1) showed that coal derived asphaltenes have a linear response of the logarithm molecular weight and retention volume when using benzene as the solvent and micro-styragel as the analytical HPLC column. There was considerable scatter in the points on the plot when one examines one process relative to another. The column was calibrated with a series of aromatic hydrocarbons and propylene glycols of known molecular weight. The asphaltene samples tested were isolated by preparative GPC techniques and the molecular weights determined by vapor pressure osmometry.

RESULTS AND DISCUSSION

Work in our own laboratory suggests that there is good reason to expect that coal and lignite derived asphaltenes and preasphaltenes may be analyzed for molecular weight using a universal calibration curve based on hydrogen content. Our data for this postulate takes two forms, solubility relationships to structure and our own GPC molecular weight analyses of a series of lignite derived asphaltenes and preasphaltenes.

(a) Solubility Relationships.

For the past several years our group has been investigating the difference between a large number of lignite derived asphaltenes and preasphaltenes (16). Over 100 different samples were obtained from the University of North Dakota Energy Research Center (UNDERC, formerly GFETC). The lignite and coal derived products were obtained under a range of temperatures from 400° to 480°C, under hydrogen or hydrogen-carbon monoxide pressures from 1500 to 4000 psi and various donor solvent conditions. The samples were fractionated into asphaltenes and preasphaltenes by solvent extraction using toluene and tetrahydrofuran (THF). The extracts were further fractionated by preparative GPC techniques. The isolated fractions were then analyzed for elemental composition, number average molecular weight by VPO using pyridine as the solvent, hydroxyl oxygen content by acetylation procedures and carbon structure by NMR techniques.

Plots of mol H/mol C, mol H/mol (O+S+N+C), and edge aromatic carbons/total aromatic carbons (H_{aru}/C_{ar}) versus acidity (mmol/g) were constructed. All the plots show a similar differentiation between the asphaltenes and preasphaltenes as illustrated in Figure 1 for mol H/mol (O+S+N+C). Figure 1 shows nearly a complete separation of the asphaltenes and preasphaltenes into two distinct regions of the graph.

From solubility parameter theory for regular solutions the activity coefficient, γ_i, for a solute i dissolving into solvent j is given by Equation 1 (17), where δ is the value of the Hildebrand solubility parameter

$$RT\ln\gamma_i = V_i(\delta_i-\delta_j)^2 \tag{1}$$

of the solvent or solute and V_i is the molar volume of the solute. For maximum solubility the activity coefficient should approach unity and thus it is desirable to have $\delta_i = \delta_j$. The rule of thumb used in organic chemistry is that 'likes dissolve likes'. The solubility regions defined by Figure 1 suggest that the ordinate, hydrogen to other elements, is a function of the π and dispersive interactions of the coal matter while the abscissa, mmoles OH/g, is a function of the hydrogen bonding. Clearly the total hydrogen and hydroxyl contents are decisive parameters for establishing the benzene or THF solubility of the coal materials.

Equation 1 predicts an increase of the solubility activity coefficient with increasing molar volume of the solute. Several attempts were made to include V in the correlations by plotting Log (H/C + MW) or Log (H/C + MW/10) versus the acidity of the samples. This approach always mixed the asphaltene and preasphaltene regions. Asphaltenes and preasphaltenes have considerable overlapping of the molecular weights although on the average the total preasphaltene sample is several hundred grams/mole higher for the same process. We did observe for a series of samples obtained from the same

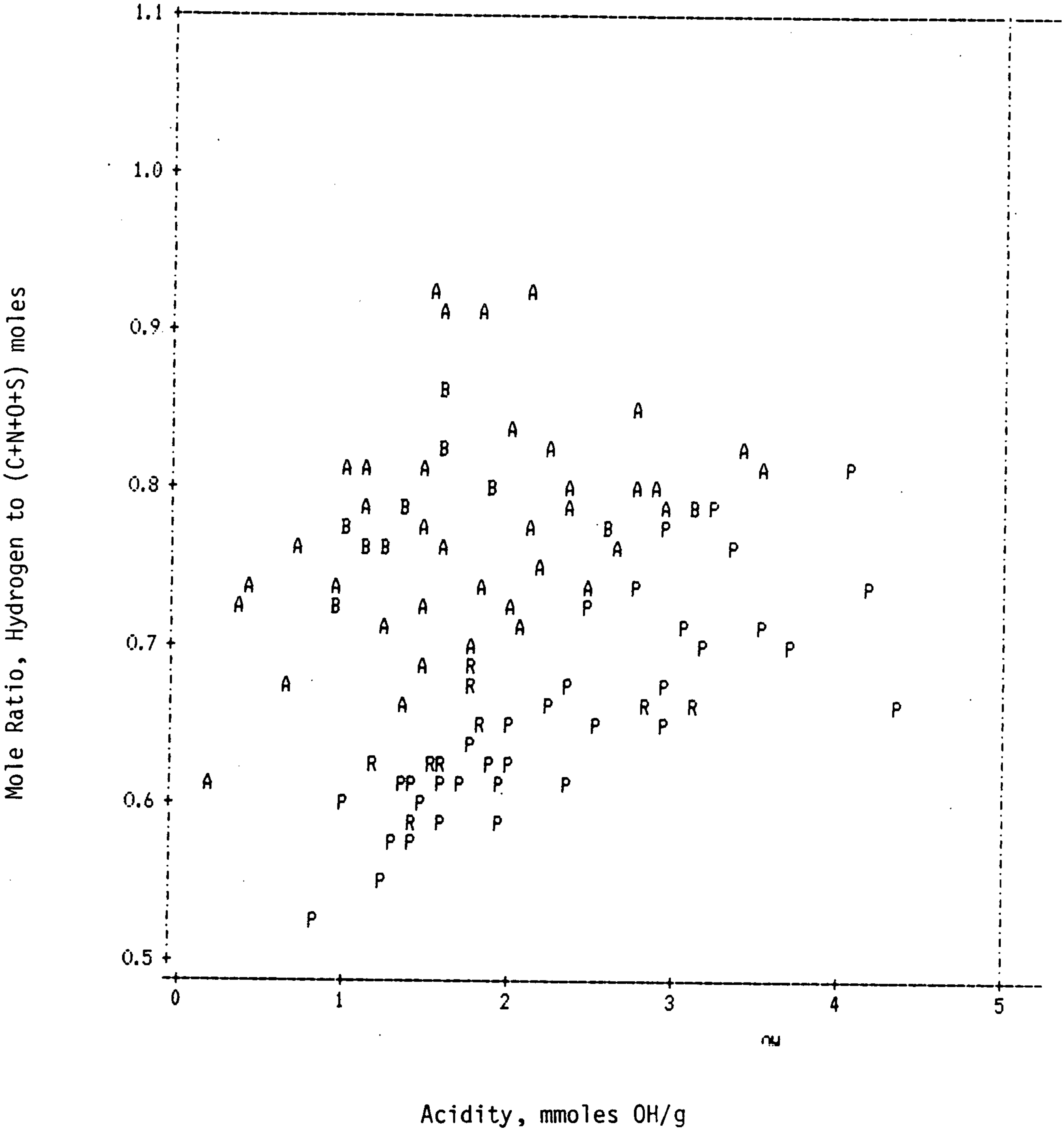

Figure 1. The hydrogen and acid content of asphaltenes (A) and preasphaltenes (P) fractions. Total preasphaltene (R) and total asphaltenes (B) are also plotted (unfractionated).

process conditions that the molecular weight increased as the H/C mole ratio decreased. Therefore the influence of molar size on the solubility is partially taken into account when the hydrogen parameter is used in such plots as Figure 1.

The solubility parameters δ_H and δ_{OH} have great impact upon the resulting hydrodynamic volume and ultimately upon the GPC response of an asphaltene or preasphaltene because the matchup with the solvent δ value will determine how well the molecule will open up or fit into the solvent. This explains the multitude of possible logarithm molecular weight versus retention time plots that one observes for different coal processes. The influence of hydroxyl content both on the δ value and possible association of the solute can be minimized by derivatization of the group to prevent hydrogen bonding. This was done in the past experiments using acetylation techniques. In the future, methylation might also be helpful. The hydrogen content could then be used in place of limiting viscosity in universal GPC calibration plots because it is a measure of such parameters as molecular volume, how the molecule spreads itself in the solvent, π-π interactions, and structural features such as shortening of the molecule due to aromatic condensation.

(b) GPC Analysis (18).

In order to test the hypothesis that the log (MW x H/C) versus retention time can be used as a calibration plot four sets of samples (41,46,32,34 runs) were analyzed by GPC techniques. The forty series samples were produced under continuous flow conditions with recycle of part of the vacuum bottoms at 460°C and nearly 100 h into the run. The thirty series were prepared at the same temperature with single passes of anthracene oil in a stirred reactor.

Analytical scale GPC analyses (HPLC) of several of the fractionated asphaltene and preasphaltene samples were carried out using three 10 nm and one 50 nm micro-styragel columns in series, with tetrahydrofuran as the mobile phase. The samples had been acetylated prior to the separations.

The determination of the number average molecular weights of the asphaltene and preasphaltene SRL fractions by vapor pressure osmometry (VPO) made it possible to establish the experimental relationships between elution volume in the analytical GPC and molecular weight. Band broadening of the peaks as shown in Figure 2 is a function of the number of theoretical plates of the column and the polydispersity of the sample. The column system was found to have 7,500 plates when using pyrene in THF. The polydispersity

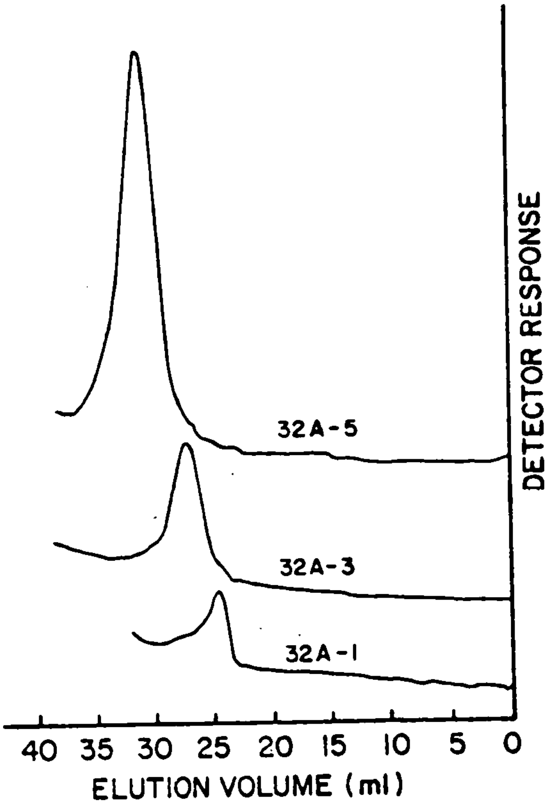

Figure 2. Typical GPC Separation

ratios (M_w/M_n) of the SRL samples were measured using commercial polystyrene for calibration of the molecular weight and retention volumes assuming a linear response. The polydispersity ratio for each of the polystyrene standards was 1.3. The range of polydispersity values of the SRL fractions was found to be 1.05 to 1.3.

Figure 3 shows the plot of the logarithm of molecular weight versus retention volume for the forty series asphaltenes (A) and preasphaltenes (P). A series of polystyrene standards (X) is added to the plot for comparison. It is clear that each solubility type falls into a special homogolous series slightly different from the other. Figure 4 shows the

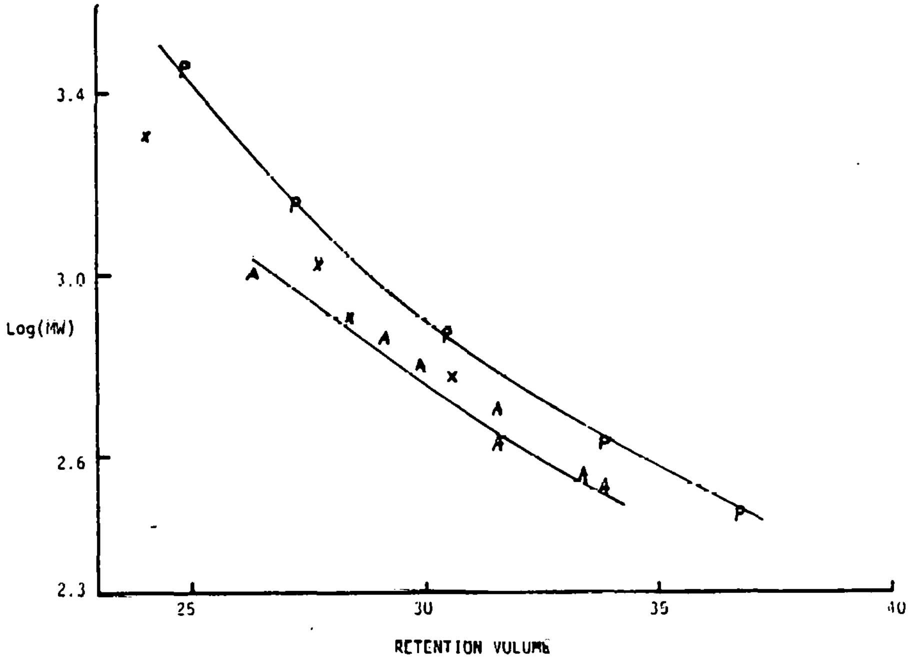

Figure 3. Logarithm Molecular Weight versus Retention Volume
X = polystyrene std., A = asphaltene, P = preasphaltene

plot of the log (MW x H/C) versus retention time for the forty series samples. The asphaltenes and preasphaltenes now fall on the same smooth curve. Polystyrene standards are added to this curve for comparison. A plot of log (MW x H_{aru}/C_{ar}) versus retention fits all the data well except that the polystyrene standards are slightly high. A plot of log (MW x X_H) versus retention volume gives a graph similar to Figure 4 with polystyrene fitting the same smooth curve (Figure 5). Figure 6 includes the lignite samples and low molecular weight models as functions of log (MW x H_H) and the retention volume. Most of the model compounds give a good fit to the data except for the phenolics which show an extreme positive deviation as indicated in Figure 6. Hydrogen bonding of these phenols to the solvent (THF) give an apparent higher molecular weight than actual solute value (18).

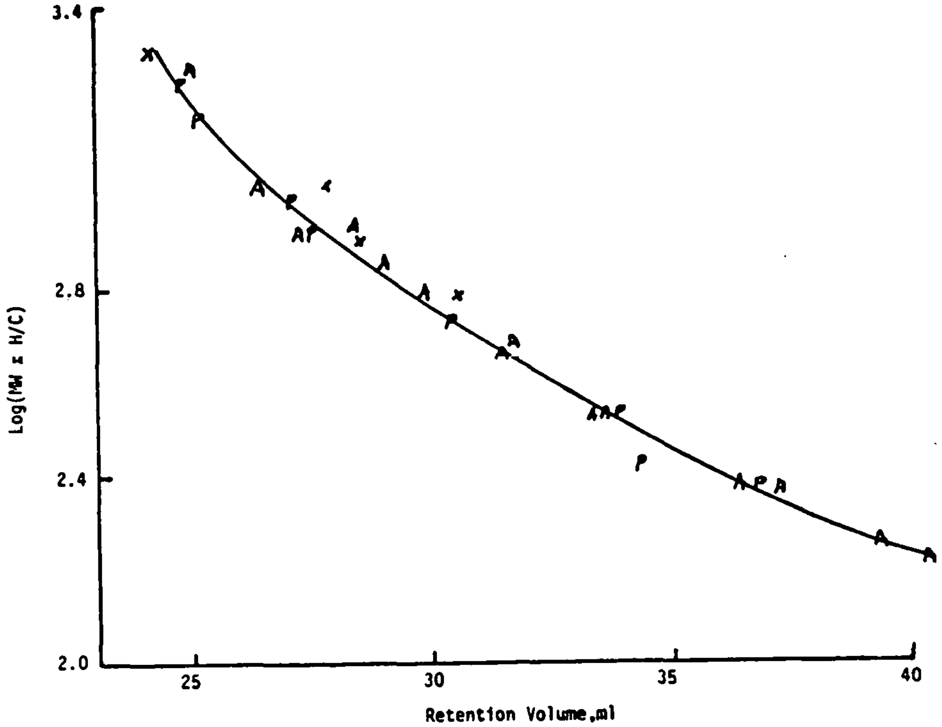

Figure 4. Logarithm (Molecular Weight x H/C) versus Retention Volume, A = Asphaltene, P = Preasphaltene, X = Polystyrene Std.

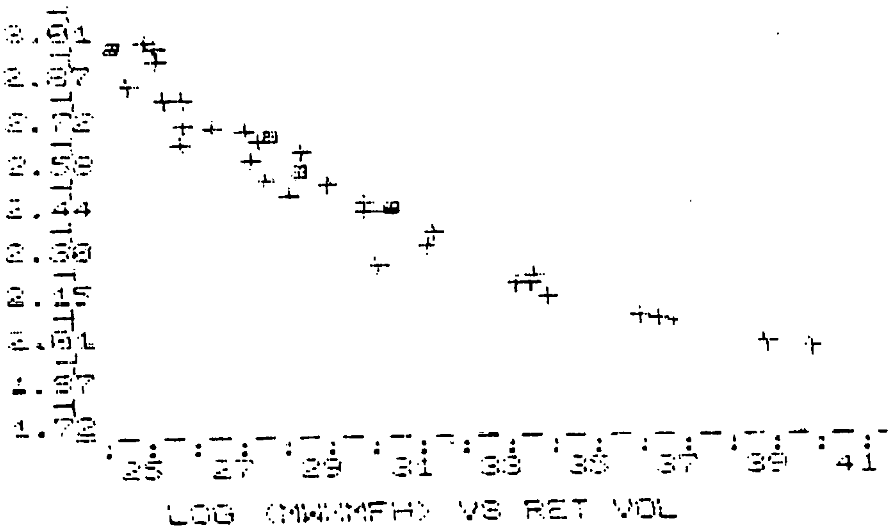

Figure 5. Logarithm (Molecular Weight x Mole Fraction H) versus Retention Volume; + = Lignite asphaltene or preasphaltene; ⊞ = polystyrene std.

In summary, the GPC data demonstrate that universal calibration plots involving the H/C, H_{aru}/C_{ar}, or X_H are good candidates for the molecular weight analyses of coal or lignite derived asphaltenes and preasphaltenes. Two of the factors, H/C or X_H, should be easier quantities to measure than limiting viscosity values of the eluent of a GPC column, while the H_{aru}/C_{ar} ratio would require NMR analysis plus elemental analysis.

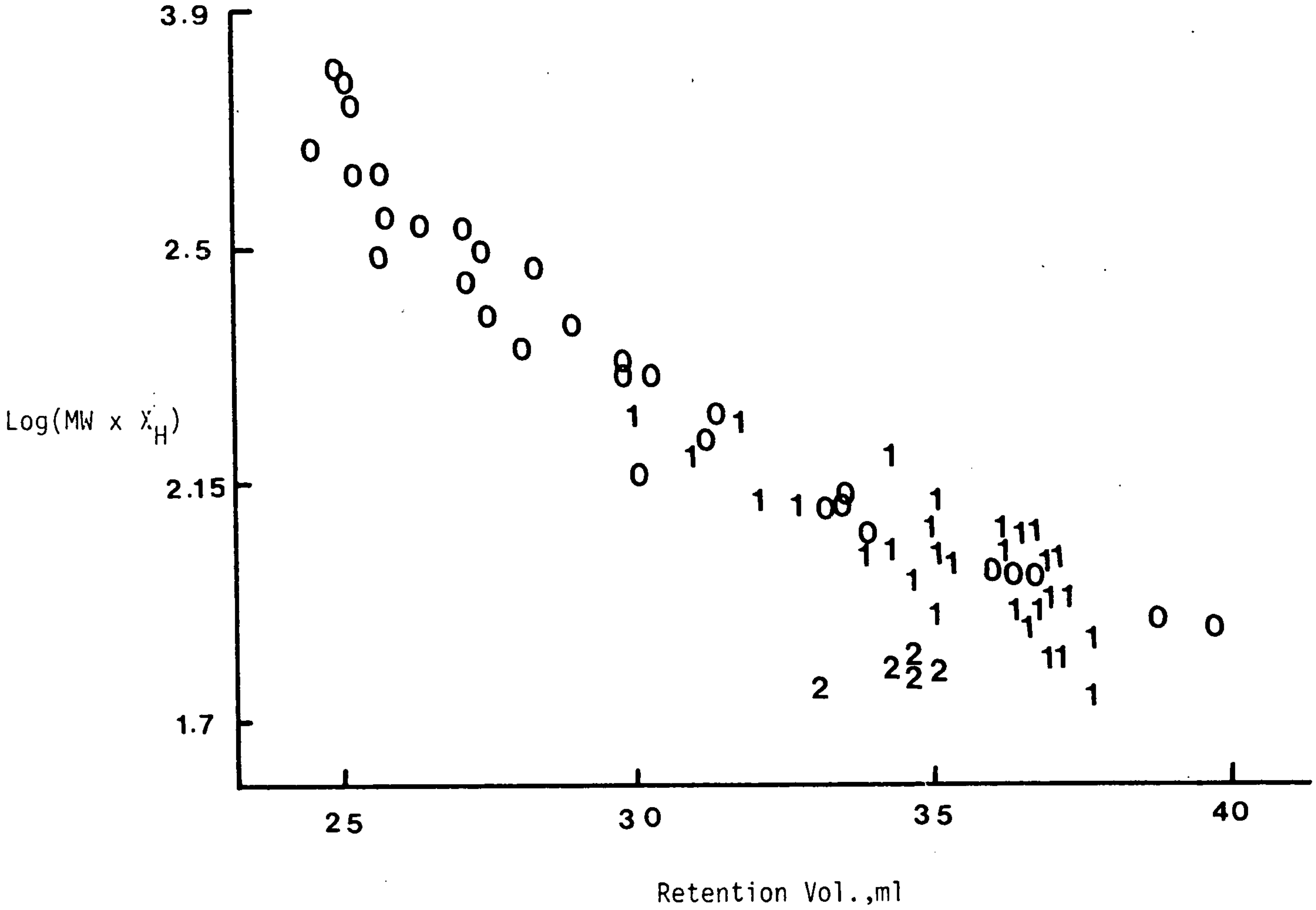

Figure 6. Logarithm(Molecular Weight x X_H) versus Retention Volume,

1 = model compounds, **0** = lignite samples, **2** = phenolics.

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