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GEL FILTRATION CHROMATOGRAPHY OF RESOLE PHENOLIC RESINS

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SUMMARY

A gel filtration chromatographic column standardization technique for a phenolic resin under a given set of operating conditions such as column, solvent and elution rate is presented. Sephacryl S-200 (high resolution) was used in this work for gel filtration chromatography fractionation of a high-molecular-weight alkaline resole phenolic resin. The individual fractions were put through the analytical column to determine their elution times. The weight-average molecular weight of each of the phenolic fractions (samples) was determined by ultracentrifuge sedimentation equilibrium methods. The chromatographic column was standardized against the readily available sodium polystyrene sulfonates. Plotted data from both the sodium polystyrene sulfonates and ultracentrifuged samples gave essentially straight lines. Subtracting the equation of the least squares line of the sodium polystyrene sulfonate from that of the phenolic gave an approximate correction factor to be added to any newly standardized sodium polystyrene sulfonate column and gives an approximate phenolic standardization without resorting to the ultracentrifuge. The standardization technique will be of interest to researchers and developers of phenolic resins and other water soluble polymers.

INTRODUCTION

The resoles (alkaline condensed, thermosetting phenol–formaldehyde condensation polymers) have been of considerable commercial importance for more than 75 years. There have been few chromatographic characterization of phenolic resins[1–5]. One study included determining the weight-average molecular weight, $\bar{M}_w$, using low-angle laser light scattering as a method of detection[6]. This procedure yields quantitative results and does not require standards of known molecular weight; however, the inability of the laser to detect low-molecular-weight polymers may impose some limitations.

The present work followed gel filtration chromatography (GFC) procedures

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developed for lignin[7] with a primary objective of finding a more practical way to determine the molecular weight of phenolic resins using available polymer standards.

EXPERIMENTAL

Apparatus

The GFC system used in this study consisted of an Isco Tris peristaltic pump connected to a Pharmacia C_{26} (70 cm × 2.6 cm I.D.) or C_{16} (analytical, 70 × 1.6 cm I.D.) chromatographic column with two adapters (AC-26 and AC-16, respectively) which contained Sephacryl [high resolution (HR)] packing material. The column was connected to a LKB S Uvicord ultraviolet detector (with a 280-nm filter) interfaced with a Nelson Analytical Chromatographic data acquisition system. Graphs were produced on a Hewlett-Packard 7550A graphics plotter.

Ultracentrifuge studies

The individual samples taken during the fractionation of the phenolic resole were frozen. Upon thawing, the samples were neutralized with a Na_2CO_3–$NaHCO_3$ buffer system such that the final concentrations were: 0.10 *M* sodium chloride, 0.10 *M* Na_2CO_3–$NaHCO_3$, and pH 9.7–10.0. The sample absorbance was near 0.5 at 285 nm. The final sample solutions contained less than 0.03 g/l of resin. Their $\bar{M}_w$ values were determined by ultracentrifuge sedimentation equilibrium monitored with a photoelectric scanner in a Beckman Spinco Model E analytical instrument[8]. $\bar{M}_w$ was calculated by using equations of Lansing and Kramer[9]. The specific volume of the phenolic resole solids was assumed to be 0.794 ml/g (specific gravity, 1.26) and independent of molecular weight.

Reagents

A phenol–formaldehyde (PF) resin was prepared in the laboratory using the Redfern cooking technique with a formaldehyde to phenol ratio of 1.86 and sodium hydroxide–phenol mol ratio of 0.4. The resin characteristics are shown in Table I.

The eluent used was 0.10 *M* sodium hydroxide (previously filtered through 0.45-μm Whatman glass fibre filters) at flow-rates of 2.0 ml/min for the C_{26} column and 1.6 ml/min for the C_{16} column.

Sephacryl S-200 (HR) was prepared according to the instructions from Pharmacia.

TABLE I

LABORATORY COOKED PHENOL–FORMALDEHYDE RESIN CHARACTERISTICS

Property	*Unit*	*Amount*
Non-volatile solids	%	40.6
pH	–	10.8
Specific gravity	–	1.1795
Gel time at 100°C	min	27.6
Alkalinity	%	5.02
Viscosity at 25°C (Brookfield)	cP	550
Free formaldehyde	%	0.05

Standards

All standards were used without further purification. Blue dextran (Sigma) with $\bar{M}_w$ *ca.* 2 000 000 and phenol (analytical grade, Mallinckrodt) with a molecular weight of 94.1 were used to determine the exclusion volume and the permeated volume, respectively. A standardization curve was determined by using sodium polystyrene sulfonate (SPS) standards having peak molecular weights ($\bar{M}_p$) of 35 000, 18 000, 8000, 4600 and 1800. These standards had polydispersities of 1.1 except for the 1800 which had a polydispersity of 1.25.

Analyses

The phenolic resin (100 mg) was loaded onto a C_{26} column and fractions were collected as reported in Table II. Each fraction was analyzed without further preparation on the C_{16} column. Because of the low polydispersities, the standards $\bar{M}_p$ are considered $\bar{M}_w$ values in the standardization calculations.

TABLE II

SAMPLING TIME AND MOLECULAR WEIGHT RANGE FOR FRACTIONS OF THE PHENOL–FORMALDEHYDE RESIN

Fraction No.	*Collection time (min)*	*Volume (ml)*	*Molecular weight range ($\bar{M}_w$)**
F-I	59.8 to 60.8 = 1.0	2.0	42 000–32 000
F-II	64.0 to 65.0 = 1.0	2.0	15 700–14 700
F-III	69.5 to 70.5 = 1.0	2.0	10 000–9700
F-IV	75.6 to 76.1 = 0.5	1.0	5299–4600
F-V	83.6 to 84.1 = 0.5	1.0	3000–2900
F-VI	90.8 to 91.3 = 0.5	1.0	2000–1900
F-VII	97.0 to 97.5 = 0.5	1.0	1000–950
F-VIII	101.9 to 102.4 = 0.5	1.0	500–470

* The $\bar{M}_w$ values are based on sodium polystyrene sulfonate standards.

RESULTS AND DISCUSSION

A phenol–formaldehyde resin was reacted to near gelation to provide samples covering a high range of phenolic molecular weights to facilitate the ultracentrifuge studies. The resin contained a formaldehyde–phenol mol ratio of 1.86 and a sodium hydroxide–phenol mol ratio of 0.40. The sodium hydroxide was added in three shots. The first shot of sodium hydroxide was added with the remainder of the reactants. The second shot of sodium hydroxide was added to the partially reacted resin, reducing the viscosity to less than 500 cP. Then the batch was cooked to a viscosity of over 2000 cP and again reduced to less than 550 cP with the third shot of sodium hydroxide. The non-volatile solids were 40.6%.

Fig. 1 shows the profile of the unfractionated resin upon elution from Sephacryl S-200 (HR) with 0.10 *M* sodium hydroxide. The size-exclusion chromatography constant K_{sec} values are used as abscissas in Figs. 2 and 3. The curves in Fig. 3 may allow the relationship of the phenolic standardization curve to be derived for other

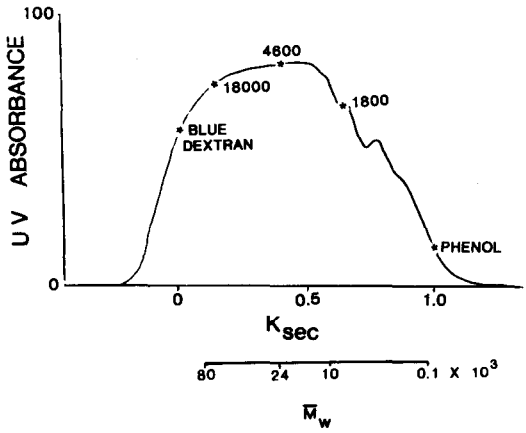
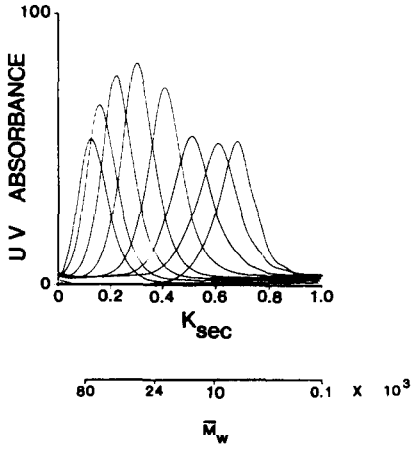


Fig. 1. Elution curve of experimental phenolic resin with 0.10 *M* sodium hydroxide on a 70 cm × 2.6 cm I.D. Pharmacia C_{26} gel filtration column. [$\bar{M}_w$ (PF) values are from ultracentrifuge determinations.]

columns and/or conditions from the easily obtained sodium polystyrene sulfonate standards.

The standardization curve with sodium polystyrene sulfonate standards allows log $\bar{M}_w$ (SPS) of the sodium polystyrene sulfonate standards to be plotted in Fig. 3 (lower curve). The ultracentrifuge results from the phenolic samples are shown in the upper curve. The relationship between these curves should remain unchanged upon repacking, change in column size, flow-rates, etc. If this relationship, indeed, remains unchanged, it will allow easy quantification of various phenolic resin studies.



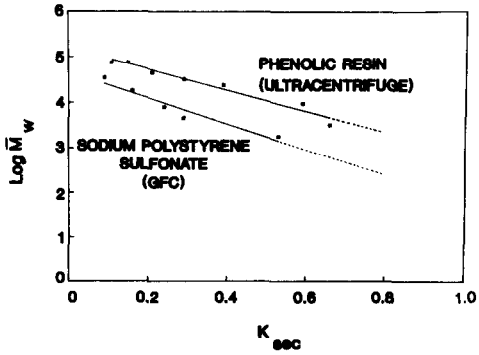


Fig. 2. Elution profiles of the fractions taken as indicated in Table II. [$\bar{M}_w$ (PF) values are from ultracentrifuge determinations.]

Fig. 3. Calibration curve of experimental phenolic resin, comparing ultracentrifuge weight-average molecular weights of fractionated samples to sodium polystyrene sulfonate standards (Table III).

TABLE III

MOLECULAR WEIGHT AND K_{sec} VALUES FOR THE SODIUM POLYSTYRENE SULFONATE STANDARDS AND THE PHENOL–FORMALDEHYDE RESIN FRACTIONS

Sodium polystyrene sulfonate standard			*Phenol–formaldehyde resin fraction*		
Standard No.	$\bar{M}_w$	K_{sec} *(GFC)*	*Fraction No.*	$\bar{M}_w$ *(ultracentrifuge)*	K_{sec} *(GFC)*
1	35 000	0.0862			
			F-I	78 008	0.1141
2	18 000	0.1552	F-II	76 403	0.1479
			F-III	44 818	0.2100
3	8000	0.2414	F-IV	32 331	0.2890
			F-V	24 017	0.3903
4	4600	0.2931	F-VI	*	0.4972
			F-VII	8741	0.5931
5	1800	0.5345	F-VIII	3220	0.6607

* Sample fraction F-VI was inadvertently polymerized, and no value is reported.

The K_{sec} value is the fractional portion of the useful range of the column at the peaks of the experimental sample. The K_{sec} of blue dextran is defined as zero since the molecules are too large to enter any of the pores. The K_{sec} of phenol is defined as 1.0 since the phenol molecules are small enough to enter all of the pores.

The K_{sec} would be calculated from eqn. 1.

$$K_{sec} = \frac{\text{sample peak elution time minus blue dextran elution time}}{\text{phenol peak elution time minus blue dextran elution time}} \quad (1)$$

Linear least squares lines on the phenolic resin (PF) fractions as determined by ultracentrifuge (UL) and sodium polystyrene sulfonates shown in Fig. 3 are expressed mathematically in eqns. 2 and 3.

$$\log \bar{M}_w\,(\mathrm{PF_{UL}}) = 5.1965 - 2.3339K_{sec} \quad (2)$$

$$\log \bar{M}_w\,(\mathrm{SPS}) = 4.6668 - 2.8343K_{sec} \quad (3)$$

Subtracting eqn. 3 from eqn. 2 gives the value to be added to a phenolic sample run on a sodium polytyrene sulfonate standard column under the given conditions (yielding the $\Delta\log \bar{M}_w$). This calculation (eqn. 4) is expressed as:

$$\Delta\log \bar{M}_w = 0.5297 + 0.5004K_{sec} \quad (4)$$

Eqn. 5 extends the calculations for a phenolic resin from a newly SPS restandardized column to actual $\bar{M}_w$ (PF) based on the ultracentrifuging of phenolic resin.

$$\log \bar{M}_w\,(\mathrm{PF}) = \log \bar{M}_w\,(\mathrm{SPS}) + \Delta\log \bar{M}_w \quad (5)$$

For a phenolic fraction (sample) with a K_{sec} of 0.3903 based on SPS standardization, the log $\bar{M}_w$ (SPS) for the resin would equal 3.5606 (from eqn. 3). The $\bar{M}_w$ (SPS) is 3636 for this resin fraction [the antilog of log $\bar{M}_w$ (SPS) = 3.5606]. For comparison, the $\bar{M}_w$ (PF) is calculated as follows (eqns. 4 through 5):

$$\Delta\log \bar{M}_w = 0.5297 + 0.5004(K_{sec} \text{ of } 0.3903) = 0.7250$$

$$\log \bar{M}_w \text{ (PF)} = \log \bar{M}_w \text{ (SPS)} + \Delta\log \bar{M}_w = 3.5606 + 0.7250 = 4.2856$$

The $\bar{M}_w$ (PF) would be 19 300 [the antilog of log $\bar{M}_w$ (PF) = 4.2856].

CONCLUSIONS

The most important objective of this project was to be able to relate both theoretical concepts and new product development in phenolics to actual molecular weights rather than to relative ones. This objective was achieved with the formulation used in the study but resins of differing mol ratios of phenol to formaldehyde, differing sodium hydroxide levels, differing processing techniques, and differing K_{sec} values all need to be tested. If these all show the same relationship between K_{sec} as was shown in this study by sodium polystyrene sulfonates, the method should have wide application, both in research and industrial manufacturing.

Another objective of this project was to have a method fast enough for industrial process control that requires an analytical time of 15 min or less. The present GFC method requires about 1 h per sample. Faster times can be obtained by use of high-performance liquid chromatography (HPLC). The problem will be in finding a suitable HPLC column that is free from artifacts, *e.g.*, hydrogen bonding, association, absorption, etc., for the phenol–sodium hydroxide system. Such work is planned for the future.

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