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SIZE EXCLUSION CHROMATOGRAPHY OF NONIONIC AND ANIONIC COPOLYMERS OF VINYLPIRROLIDONE

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ABSTRACT

Size exclusion chromatography (SEC) of poly(vinylpyrrolidone-co-vinylacetate), PVPVA, and poly(vinylpyrrolidone-co-dimethylaminoethylmethacrylate-co-vinylcaprolactam), PVPDMAEMAVC, is evaluated in terms of resolution between polymer and solvent peaks using aqueous and nonaqueous mobile phases. A 1:1 (v/v) water/methanol, 0.1M LiNO₃ mobile phase is used with four Waters Ultrahydrogel columns with pore sizes of 120Å, 500Å, 1000Å, and 2000Å. DMF, 0.1M LiNO₃ mobile phase is used with three different two column sets. Two of the column sets are comprised of a mixed bed packing of poly(styrene-co-divinylbenzene), obtained from Shodex (KD80M), followed by either an Ultrahydrogel 120Å or a PLgel 100Å. The third two column set is a PLgel 10⁴Å followed by a PLgel 500Å. Any of the second columns in these sets improve separation between the trailing end of the polymer peak and the leading end of the solvent peak but the column set using an Ultrahydrogel 120Å yields a separation of these peaks whose valley is closer to the baseline. The aqueous mobile phase with the four column set yields a separation between the trailing end of the polymer peak and the leading end of the solvent peak whose valley is closest to the baseline. Recovery of PVPVA and PVPDMAEMAVC from the columns evaluated is 100%. Vinylpyrrolidone compositions of PVPVA ranging from 30 to 70 mole % were studied using both mobile phases. SEC of

poly(vinylpyrrolidone-co-acrylic acid), PVPAA, is reported using the four Waters Ultrahydrogel columns above with 0.1M TRIS buffer, pH 9, 0.2M LiNO₃. Vinylpyrrolidone compositions of PVPAA ranging from 25 to 90 mole % were studied. Polymer recovery is 100%.

INTRODUCTION

In a previous study, weight average molecular weights of cationic copolymers, quaternized poly(vinylpyrrolidone-co-dimethylaminoethylmethacrylate), PVPDMAEMA, determined by both universal calibration and size exclusion chromatography/low angle laser light scattering, SEC/LALLS, were found to be in good agreement.¹ The SEC conditions using a 0.1M TRIS, pH 7 buffer, 0.5M LiNO₃ mobile phase on Waters Ultrahydrogel columns were found to cause elution of PVPDMAEMA based on hydrodynamic volume. Also reported² by this laboratory was the separation by hydrodynamic volume of nonionic homopolymers of poly(vinylpyrrolidone), PVP, on Toyo Soda TSK-PW columns (equivalent to Waters Ultrahydrogel columns) using a mobile phase of 1:1 water/methanol containing 0.1M LiNO₃. This mobile phase, previously reported³, was used to yield a log-linear molecular weight separation⁴ of PVP spanning over three decades (10⁵ to 10⁸ g/mol).

In the present work, SEC for nonionic copolymers poly(vinylpyrrolidone-co-vinylacetate), PVPVA, and poly(vinylpyrrolidone-co-DMAEMA-co-vinylcaprolactam), PVPDMAEMAVC, is evaluated using different columns with aqueous and nonaqueous mobile phases. SEC is also investigated for an anionic copolymer, poly(vinylpyrrolidone-co-acrylic acid), PVPAA, using an aqueous mobile phase.

EXPERIMENTAL

PVPVA, PVPDMAEMAVC, and PVPAA, all synthesized by free radical polymerization, were produced by GAF Chemicals Corporation. PVPVA samples were obtained in the following form: a 50% solution in ethanol, E series; a 50% solution in isopropanol, I series; a 50%

solution in water, W series; and a free flowing powder, S series. Vinylpyrrolidone compositions of PVPVA were expressed by the first digit of the sample grade label. For example, PVPVA sample grade 1535, is 50 mole % vinylpyrrolidone, in isopropanol, and PVPVA sample grade E735 is 70 mole % vinylpyrrolidone, in ethanol. Vinylpyrrolidone compositions of PVPVA ranging from 30 to 70 mole % were studied. PVPAA samples were obtained as a free flowing powder. PVPAA samples grades studied, 1005, 1004, 1001, and 1030, had 25, 50, 75, and 90 mole % vinylpyrrolidone, respectively. PVPDMAEMAVC samples were obtained as a 37% solution in ethanol. The composition and synthesis of this polymer has been discussed in an earlier GAF patent.⁴ Single lots of each grade of the three polymers were used in the present work.

Polymer samples were prepared as 0.1% (w/v) solutions in their respective mobile phases by dissolution for 1/2 day on a slowly rotating wheel. For PVPVA, SEC conditions were investigated using both aqueous and nonaqueous mobile phases. A 1:1 water/methanol (v/v), 0.1M LiNO₃ solution (to be referred to as water/methanol mobile phase), or a dimethylformamide (DMF), 0.1M LiNO₃ solution (to be referred to as DMF mobile phase) was used. For the water/methanol mobile phase, four Waters Ultrahydrogel columns of pore sizes 120Å, 500Å, 1000Å, and 2000Å were connected in series. This four column set will be referred to as U4. For the DMF mobile phase, three different two column sets were used. These three column sets, Shodex KD80M plus Ultrahydrogel 120Å, Shodex KD80M plus PLgel 100Å, and PLgel 10⁴Å plus PLgel 500Å will be referred to as SU2, SP2, and PP2, respectively. The procedure of adding a Waters Ultrahydrogel column in series after a PLgel column was recently reported.⁵ For PVPDMAEMAVC, SEC conditions were evaluated also using the same columns and corresponding mobile phase used for PVPVA. For PVPAA, 1% (w/v) solutions in 0.25N NaOH were first prepared since the polymer dissolves readily in this alkaline solution. The alkaline PVPAA solutions were then diluted 1:9 (v/v) using 0.1M tris(hydroxymethyl)aminomethane (TRIS), 0.2M LiNO₃, adjusted to pH 9 with HNO₃. This TRIS solution (to be referred to

as pH 9 mobile phase) was used in conjunction with the U4 column set for SEC of the PVPAA samples.

Intrinsic viscosity, $[\eta]$, for the polymers was determined at 25°C using a 0.63 mm Ubbelohde viscometer with the solvents employed as mobile phases for the SEC experiments. For PVPVA, PVPAA, and PVPVADMAEMAVC in aqueous solution, concentrations between 1.0 and 0.2 g/dl were used to determine $[\eta]$ from a multi-point extrapolation. In order to determine $[\eta]$ for PVPVA in nonaqueous solution, a single concentration was used. $[\eta]$ was calculated using

$$[\eta] = \frac{(2(\eta_{sp} - l\eta_r))^{1/2}}{c} \quad (1)$$

where η_{sp} is specific viscosity, $l\eta_r$ is inherent viscosity, and c is concentration. Equation 1 was derived by subtracting

$$\frac{l\eta_r}{c} = [\eta] + k''[\eta]^2c \quad (2)$$

Equation 2, reported by Kraemer⁴, from

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c \quad (3)$$

Equation 3, reported by Huggins¹, and substituting $k' - k'' = 1/2$. Single point $[\eta]$ was found to be the same as $[\eta]$ determined from multi-point extrapolation for two PVPVA copolymer compositions.

The SEC apparatus included a Waters model 715 or 710B WISP auto injector, a Waters model 590 pump, and a Waters model 410 differential refractometer. Column oven temperatures were controlled at 30°C for the aqueous SEC experiments and at 40°C for the nonaqueous SEC experiments. Injection volumes were typically 100 μ l. Detector signals were collected on a DEC MINC-11 computer. Molecular weight information was obtained from the acquired data using GPC3 software from Chromatix, Inc. Eight polyethylene oxide (PEO) standards from Toyo Soda and Polymer Laboratories, with molecular weights between 860,000 and 7,100 g/mol, were used in all SEC experiments. These standards had polydispersities, (M_w/M_n), between 1.02 and 1.10.

RESULTS and DISCUSSION

The dependence of retention volume with molecular weight for PEO standards in DMF using the SU2 column set is shown by curve a in Figure 1. A good linear correlation was obtained. Elution of the PEO standards on the SP2 and the PP2 column sets also yielded a similar dependence of retention volume with molecular weight. Curve b in Figure 1 shows the dependence of retention volume with molecular weight for PEO standards in water/methanol using the U4 column set. A good linear correlation was obtained. It is important to note that the elution of PEO standards from the two column sets occurred at earlier times and at faster rates as compared to the elution of standards on the U4 set. Figure 2 shows

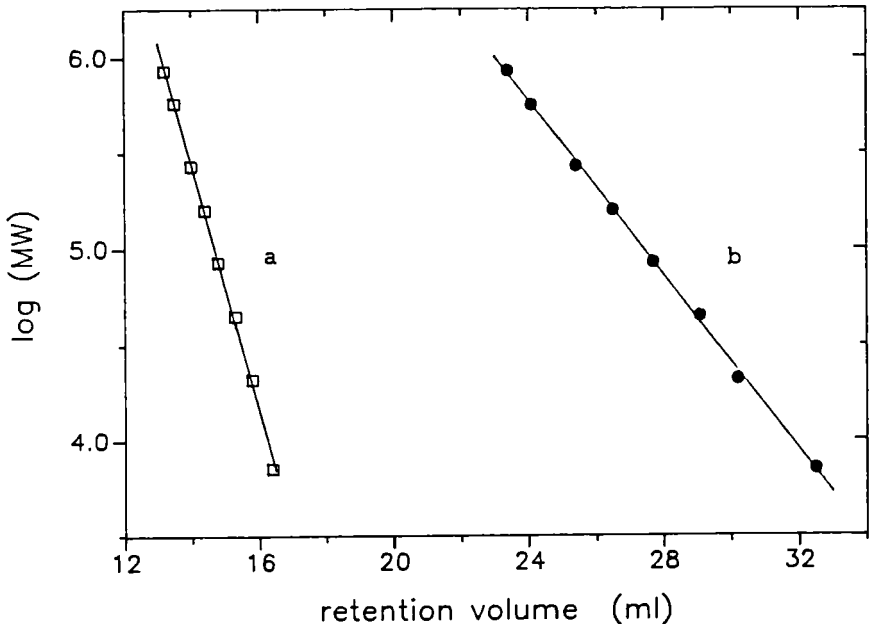


FIGURE 1 Linear fitted data of $\log(MW)$ versus retention volume for PEO standards using: a) SU2 column set with DMF solvent. b) U4 column set with water/methanol solvent.

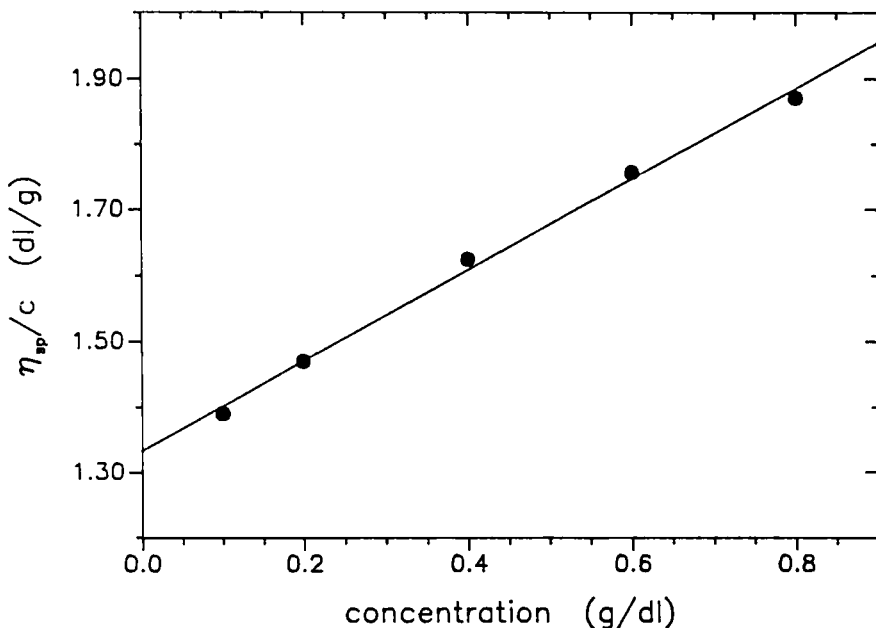


FIGURE 2 Linear fitted data of reduced viscosity versus concentration for PVPAA 1001, pH 9, 0.2M LiNO₃.

a typical graph of fitted viscosity data obtained for the polymers studied in aqueous solution. Figure 2 is a graph of η_{sp}/c versus concentration for PVPAA 1001, pH 9, 0.2M LiNO₃.

Table 1 shows weight average molecular weights, \bar{M}_w , obtained by SEC for PVPDMAEMA VC and PVPVA with various copolymer compositions studied using the four different column sets with aqueous and nonaqueous mobile phases. PVPVA and PVPVADMAEMA VC recovery were 100% from all of the columns sets. There is not necessarily any correlation between \bar{M}_w and copolymer composition. Also shown in Table 1 are $[\eta]$ values for these polymers which show the generally expected increase in $[\eta]$ with an increase in \bar{M}_w .

Figure 3 shows SEC traces, overlaid, of PVPVA 1 series obtained using the SU2 column set with DMF mobile phase. The shapes of these chromatograms are typical of the chromatograms obtained

Table 1

Weight average molecular weight^f determined by SEC using aqueous and nonaqueous solvents for PVPDMAEMAVC and various copolymer compositions of PVPVA (see Experimental section for descriptions of copolymer compositions, solvents and columns). Intrinsic viscosity of these polymers determined using the corresponding solvents used for SEC.

Polymer	Aqueous Solvent		Nonaqueous Solvent			
	Column Set		Column Set			
	U4		SU2	SP2	PP2	
	\bar{M}_w	$[\eta]$ (dl/g)	\bar{M}_w	\bar{M}_w	\bar{M}_w	$[\eta]$ (dl/g)
PVPVA:						
E335	28,800	0.265	37,900	36,700	45,000	0.261
E535	36,700	0.363	38,700	38,300	44,500	0.241
E635	38,200	0.330	37,600	37,500	45,100	0.253
E735	56,700	0.429	52,200	52,200	53,800	0.310
I335	12,700	0.176	15,000	16,700	16,000	0.162
I535	19,500	0.222	20,300	22,200	21,600	0.174
I735	22,300	0.261	21,500	24,000	21,400	0.182
W735	27,300	0.265	25,000	27,800	30,600	0.238
S630	51,000	0.424	48,600	49,300	56,000	0.321

PVP-						
DMAEMAVC	82,700	0.620	68,200	73,500	101,000	0.480

^f \bar{M}_w relative to PEO standards.

from the various compositions of PVPVA and PVPDMAEMAVC studied using the SU2 column set. Of the three column sets investigated for the polymers, SU2, SP2, and PP2, the SU2 column set yielded a separation between the trailing end of the polymer peak and the leading end of the solvent peak whose valley was closest to the baseline. Because none of these column sets achieved a satisfactory resolution in the low molecular weight range, values of \bar{M}_n were not reproducible, usually with errors greater than 5%. For the polymers studied, the three column sets all yielded chromatograms with low molecular weight shoulders, which are evident in Figure 3.

Figure 4 shows SEC traces of the PVPVA I series obtained using the U4 column set with water/methanol mobile phase and these

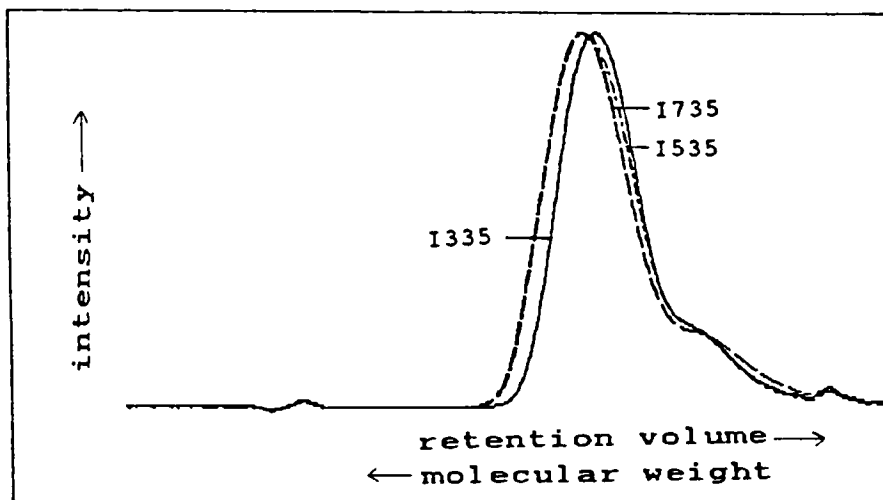


FIGURE 3 SEC traces of PVPVA, I series, using the SU2 column set with DMF solvent.

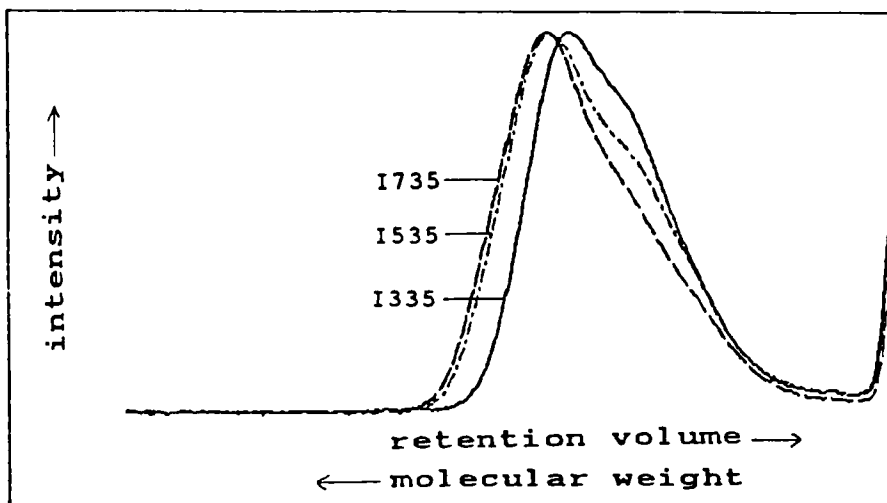


FIGURE 4 SEC traces of PVPVA, I series, using the U4 column set with water/methanol solvent.

chromatograms are typical of the chromatograms obtained from the various compositions of PVPVA and PVPDMAEMAVC studied. In comparison of the chromatograms obtained using water/methanol mobile phase with chromatograms obtained using DMF mobile phase (Figure 3) with the corresponding column sets, the U4 column set using water/methanol mobile phase yields a separation between the polymer and solvent peak whose valley is closer to the baseline. Therefore, in comparison of SEC results achieved using either the water/methanol or DMF mobile phase with the corresponding column set, the U4 column set with the water/methanol mobile phase yielded the best separation between polymer and solvent peaks. The water/methanol mobile phase with the U4 column set also yielded chromatograms with low molecular weight shoulders similar to the chromatograms obtained using DMF mobile phase with the three two column sets.

Table 2 shows \bar{M}_w obtained by SEC for PVPAA with various copolymer compositions studied using the U4 column set with pH 9 mobile phase. Figure 5 shows SEC traces, overlaid, of four copolymers. The chromatograms are reasonable but a baseline separation between the low molecular weight end of the polymer peak

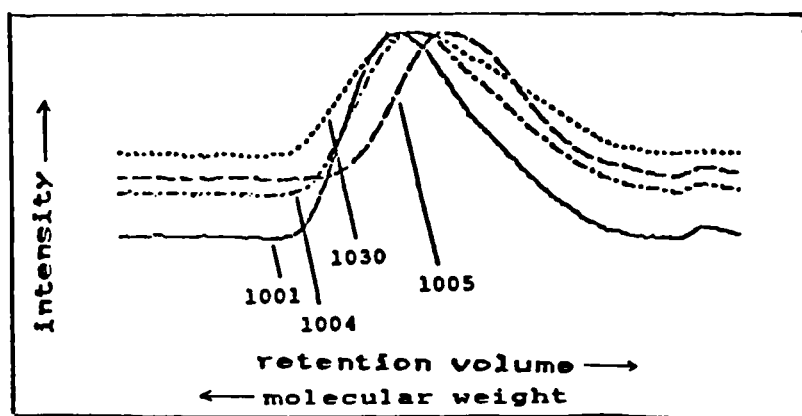


FIGURE 5 SEC traces of PVPAA copolymers using the U4 column set with pH 9 solvent.

Table 2

Weight average molecular weight^f determined by SEC using 0.1M TRIS buffer, pH 9, 0.2M LiNO₃, for various compositions of PVPAA (see Experimental section for descriptions of copolymer compositions and columns). Intrinsic viscosity of these polymers using the solvent used for SEC.

<u>PVPAA</u>	<u>\bar{M}_w</u>	<u>$[\eta]$ (dl/g)</u>
1005	135,000	1.04
1004	256,000	1.37
1001	318,000	1.33
1030	277,000	----

^f \bar{M}_w relative to PEO standards.

and the solvent peak could not be achieved. Also shown in Table 2 are $[\eta]$ values which show the generally expected increase in $[\eta]$ with an increase in \bar{M}_w . The determination of intrinsic viscosity for PVPAA 1030 was hampered by the apparent insolubility of this polymer in 0.25M NaOH at a concentration greater than 4 g/dl.

CONCLUSIONS

It was found that the most satisfactory size exclusion chromatography results for various compositions of poly(vinylpyrrolidone-co-vinylacetate) and poly(vinylpyrrolidone-co-dimethylaminoethylmethacrylate-co-vinylcaprolactam) were achieved using a Waters Ultrahydrogel four column set with a 1:1 water/methanol, 0.1M LiNO₃ mobile phase. SEC results were evaluated in terms of resolution between polymer and solvent peaks using columns from Waters, Polymer Laboratories, and Shodex with aqueous and nonaqueous mobile phases. SEC results are also reported for compositions of poly(vinylpyrrolidone-co-acrylic acid) using the four Waters Ultrahydrogel columns with 0.1M TRIS buffer, pH 9, 0.1M LiNO₃.

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