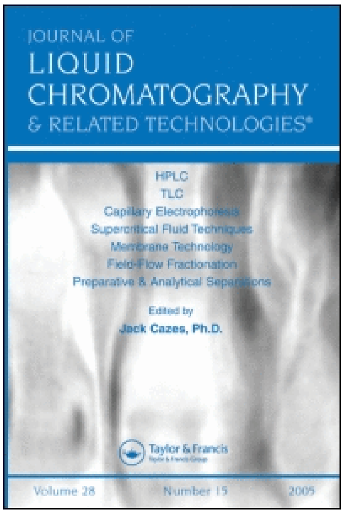

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Yoshiyuki Mukoyama[a]; Sadao Mori[b]
[a] Research and Development Department Goi Works Hitachi Chemical Company 14, Chiba, Japan [b] Department of Industrial Chemistry Faculty of Engineering, Mie University Tsu, Mie, Japan

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COMBINATION OF SIZE EXCLUSION AND ADSORPTION PHENOMENA ON A HYDROPHILIC POLYMER GEL COLUMN USING ORGANIC SOLVENTS

YOSHIYUKI MUKOYAMA[1] AND SADAO MORI[2]
[1]*Research and Development Department*
Goi Works
Hitachi Chemical Company
14, Goi-minami-kaigan
Ichihara-shi
Chiba 290, Japan
[2]*Department of Industrial Chemistry*
Faculty of Engineering
Mie University
Tsu, Mie 514, Japan

ABSTRACT

Elution behavior of alkylbenzenes, phthalate esters, oligostyrenes, and prepolymers of epoxy resins and methylated melamine-formaldehyde resins has been investigated on a column packed with hydrophilic polyhydroxyethyl methacrylate gels using tetrahydrofuran (THF), methanol, and mixtures of THF and methanol or n-hexane as the mobile phases. Size-exclusion effect was predominant when THF was used as the mobile phase and adsorption interactions between solutes and the gels superimposed the size-exclusion effect when methanol or mixtures of THF and methanol or n-hexane was the mobile phase. The gel-THF system was assumed to be SEC. The addition of methanol or n-hexane to THF in the mobile phase retarded the elution of solutes. The combination of size exclusion and adsorption modes in the same column was possible by changing composition of the mobile phase and resolution of some peaks was improved than by SEC alone. The peak identification by the present system is also improved than by SEC.

INTRODUCTION

Hydrophilic polymer gels such as polyhydroxy methacrylate gels and polyvinyl alcohol gels are now commercially available and are used exclusively for aqueous size exclusion chromatography (ASEC). The primary purpose for SEC is to estimate molecular weight of a solute, and a calibration curve of log molecular weight and retention volume has to be constructed in advance. In SEC, substances which have the same moleclular size are in general supposed to elute at the same retentin volume. Size exclusion is the main separation mode in SEC and secondary effects such as adsorption interactions between the stationary phase and solutes should be prevented from. In ASEC with hydrophilic polymer gels, secondary effects are sometimes observed and organic solvents are added to the aqueous mobile phase to minimize these effects. However, the addition of organic solvents is mostly prohibited because of gel shrinkage in a column. Only small amounts of organic solvents can be added to the aqueous mobile phases.

Porous polymer gels have attracted the attention to their stability with aqueous mobile phases over a wide range of pH. In addition, some of porous polymers such as polystyrene (PS) gels have been used in both reversed-phase and normal-phase chromatography and also in SEC with various mobile phases[1,2]. Separation of solutes by two separation modes in the same column has been reported using PS gels[3]. Prices of SEC columns are high comparing with columns used for other HPLC modes. Besides the problem of price, different types of packing materials have to be used for ASEC and non-aqueous SEC, respectively: ASEC with hydrophilic polymer gels and non-aqueous SEC with hydrophobic polymer gels. It must be very economical if one can use the same column for SEC with non-aqueous solvents and ASEC with aqueous solvents in addition to normal- and reversed-phase chromatography without any loss of column efficiency.

Recently, it was found that some polyvinyl alcohol gels were compatible with polar and non-polar organic solvents[4] and ASEC with H_2O and SEC with chloroform in the same column were reported[5]. Elution behavior of oligostyrenes and prepolymers of epoxy resins, methylated melamine-formaldehyde resins, and phenol-formaldehyde resins has also been examined in the mobile phases of chloroform, methanol and their mixtures[6].

One of the authors (Y.M.) has succeeded in producing polymethacrylate gels having hydrophilic pendant groups for ASEC and found that these gels were also compatible with organic solvents. In this work, mixtures of tetrahydrofuran (THF) and methanol or n-hexane were used as the mobile phases and the elution behavior of several organic compounds were investigated on a column packed with these hydrophilic gels. Separation of several prepolymers of epoxy resins and methylated melamine-formaldehyde resins were also discussed.

EXPERIMENTAL

A Gelpak GL-W520 column (300 mm x 10.7 mm i.d.)(Hitachi Chemical Co., Ltd., Shinjuku-ku, Tokyo 160, Japan) packed with polymethacrylate gels having hydrophilic pendant groups was used in this experiment. The packing solvent was methanol which was displaced with deionized water containing 0.02% sodium azide after the gels being packed. The exclusion limit of this column was 6000 as pullulan molecular weight. The number of theoretical plates (N) was 14000 plates per 300 mm by injecting 0.02 ml of a 1% ethylene glycol solution at a flow rate of 1 ml/min of the mobile phase (water). The original solvent in the column, water, was replaced to methanol at a flow rate of 0.3 ml/min. The value of N in the mobile phase of methanol was 13100 plates by injecting 0.1 ml of a 0.1% isopropylbenzene solution at a flow rate of 1 ml/min. After replacing the solvent in the column from methanol to THF at a flow rate of 0.3 ml/min, the value of N in the mobile phase of THF was 10500 plates by injecting 0.1 ml of a 0.1% isopropylbenzene solution at a flow rate of 0.5 ml/min.

A high-performance liquid chromatograph Model TRIROTAR (Japan Spectroscopic Co., Ltd., Hachioji, Tokyo 192, Japan) was used with an ultraviolet (UV) detector Model UVIDEC-100 II operated at 254 nm. Mobile phases were mixtures of THF and methanol and of THF and n-hexane and elution was performed in the isocratic mode at a flow rate of 0.5 ml/min. The concentration of the sample solutions was 0.1% and the value of the sample solution injected was 0.1 ml. Samples were dissolved in the solvent used as the mobile phase.

The samples were alkylbenzenes, phthalate esters, oligostyrenes, and prepolymers of epoxy resins and methylated melamin-formaldehyde resins.

RESULTS and DISCUSSION

Retention volumes and peak widths of alkylbenzenes and phthalate esters in THF and methanol are listed in Table I. Elution of solutes in both cases was in order of decreasing molecular weight, that is, solutes of higher molecular weight eluted earlier. Peak width decreased with decreasing retention volume of solutes (with increasing molecular weight) except dodecylbenzene and di-n-decyl phthalate. Retention volumes of each solutes in the mobile phase of methanol were larger and peak widths were broader than those in the mobile phase of THF. However, the value of N in the mobile phase of methanol is larger than that in THF (see EXPERIMENTAL section). This is because of the increase in retention volume of each solute in addition to the increase in peak width in methanol. Adsorption interactions between solutes and the gels may superimpose the size-exclusion effect when methanol is used as the mobile pahse.

The shift in the retention volumes of benzene, dimethyl phthalate (DMP), and di-2-ethylhexyl phthalate (dioctyl phthalate,

TABLE I

Retention Volume and Peak Width of Alkylbenzenes and Phthalate Esters in Tetrahydrofuran and Methanol

Sample	Mobile phase			
	Methanol		Tetrahydrofuran	
	V_R ml	Peak width ml	V_R ml	Peak width ml
Benzene	25.2	1.11	19.1	0.85
Ethylbenzene	24.0	0.88	17.7	0.72
n-Butylbenzene	23.2	0.83	16.75	0.66
n-Hexylbenzene	22.7	0.83	16.10	0.63
n-Octylbenzene	22.3	0.84	15.60	0.60
Dodecylbenzene	20.8	1.39	15.00	0.65
Dimethyl phthalate	28.5	1.08	19.8	0.79
Diethyl phthalate	25.1	0.87	17.9	0.70
Di-n-propyl phthalate	23.9	0.84	16.9	0.61
Di-n-butyl phthalate	23.2	0.88	16.2	0.59
Di-n-heptyl phthalate	21.7	1.01	14.9	0.57
Di-n-nonyl phthalate	20.7	0.82	14.4	0.55
Di-n-decyl phthalate	20.6	1.09	14.1	0.65

DOP) with changing in composition of the mobile phase were determined and the results are shown in Figure 1. The minimum retention volumes of these solultes were obtained at the mobile phase compositions between THF-n-hexane (90:10,v/v) and THF-methanol (80:20,v/v), depending on the solutes.

According to a theory to elucidate the elution mechanism of size exclusion plus secondary effects, a concept of a solubility parameter can be applied[2]. When the solubility parameter of the mobile phase is equal to that of the gel or a solute, then the separation occurs mainly by size-exclusion effect. In other cases, secondary interactions such as adsorption or partition phenomena must superimpose the size-exclusion effect, or an extreme case is that adsorption or partition phenomena are predominant for separation of solutes. This theory can be applied to non-ionic substances for solutes, gels, and solvents.

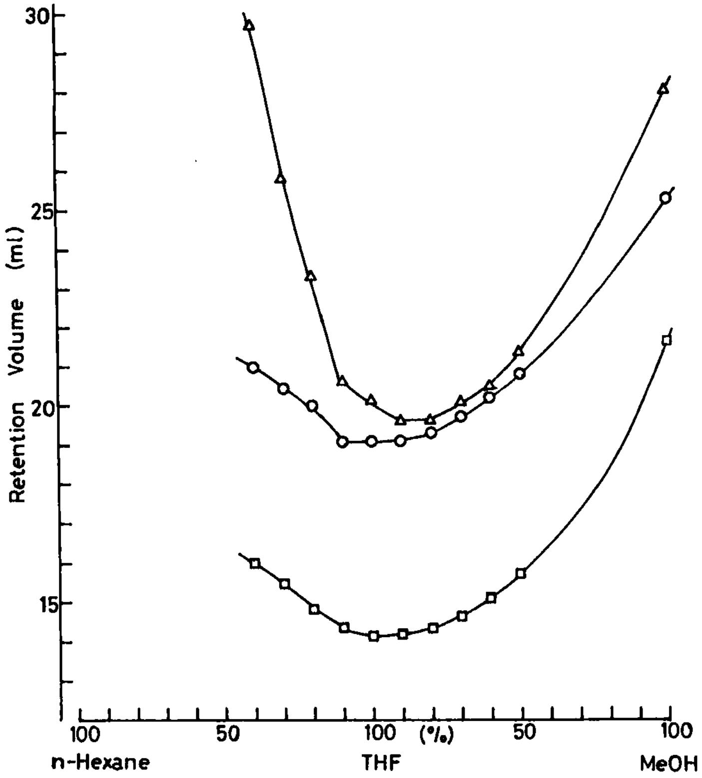

FIGURE 1. Retention volume of solutes vs composition of the mobile phase. (o) Benzene, (△) dimethyl phthalate, (□) di-n-decyl phthalate.

Although polyhydroxyethyl methacrylate gels used in this work is non-ionic polymer gels, hydrogen bonding of carbonyl groups of methacrylate polymers with silanol groups on silica gel has been observed[7]. Qualitative treatments may be possible by knowing the solubility parameters of the mobile phases and the solutes. In Figure 1, the solubility parametes of the mobile phases of THF-n-hexane (90:10), THF, THF-methanol (90:10 and 80:20) are neary equal to those of solutes (benzene, DMP, and DOP), and the separation in these systems was mainly achieved by size exclusion.

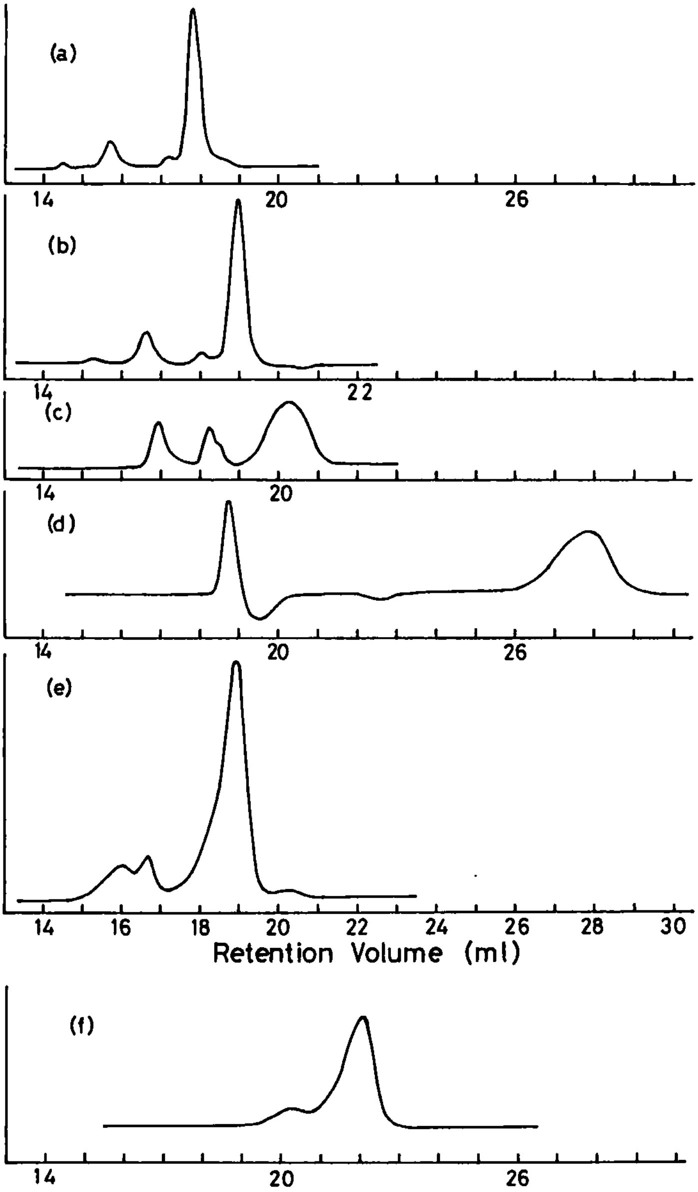

FIGURE 2. Chromatograms of epoxy resin prepolymer EPIKOTE 828. Mobile phase: (a) THF, (b) THF-methanol (75:25), (c) (50:50), (d) (25:75), (e) THF-n-hexane (90:10), (f) (80:20), (g) (70:30), (h) (65:35), (i) (60:40). Attenuation: x0.64 AUFS.

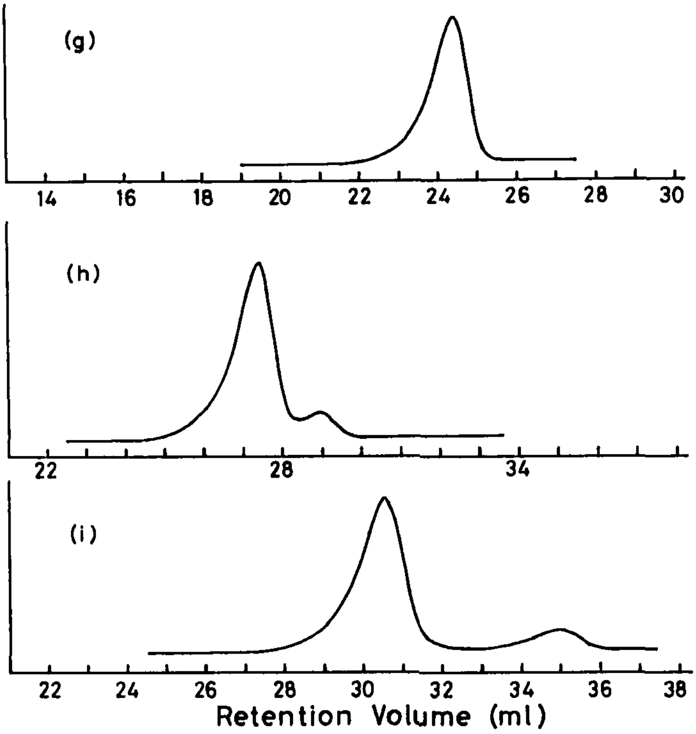

FIGURE 2. (Continued from the previous page.)

With increasing n-hexane content or methanol content in the mobile phase, adsorption or partition effects superimposed the size-exclusion effect and retention volumes of these solutes increased. Because of the capability of hydrogen bonding of the gels with solutes, the reverse order of elution for solutes between the mobile phases of THF-n-hexane and THF-methanol was not observed unlike the results of PS gels[2].

Figure 2 is the chromatograms of epoxy resin prepolymers EPIKOTE 828. The mobile phase in Figure 2(a) was THF. The shape of the chromatogram was similar to that in a PS gel-THF system[8] and the separation mode is assumed to be size exclusion.

The addition of methanol to THF in the mobile phase retarded the elution of epoxy resin prepolymers (Figure 2 b - d). Furthermore, the chromatogram of EPIKOTE 828 was divided into two peaks when the composition of the mobile phase was THF-methanol (27:75), one eluted at 19 ml and the other (the main peak) at 28 ml. The first peak may be polar substances such as dihydroxy oligomers and the second one must be less polar. The addition of n-hexane to THF also retarded the elution (Figure 2 e - i) and when the content of n-hexane was 30% (Figure 2 g), only one peak was observed. The elution order of the main peak to the minor peak was reversed when the content of n-hexane in the mobile phase was more than 35% (Figure 2 h and i). The first peak (the main peak) in Figure 2 i includes less polar substances and the minor peak contains polar substances.

Chromatograms of epoxy resin prepolymer EPIKOTE 1001 are shown in Figure 3. Resolution of the sample in THF (Figuare 3 a) is better than that in a PS gel/THF system[8]. The addition of methanol up to 25% increased the resolution of the sample. Peaks appeared at V_R = 15.7 ml and 17.8 ml in Figure 3 (a) were supposed to be the same metrials appeared at the same retention volumes in Figure 2 (a) by SEC[8]. However, the retention volumes of the peaks in Figure 3 (b) and (c) were different from those in Figure 2 (b) and (c). Therefore, the present system is very valuable for peak identification than a PS gels-THF system (SEC). The addition of n-hexane to THF in the mobile phase retarded the elution of the each oligomers in the sample (Figure 3 d - g). These peaks concentrated in one peak at V_R = 24 ml in the mobile phase of THF-n-hexane (70:30)(Figure 3 f) and then eluted in the order of increasing molecular weight in the mobile phase of THF-n-hexane (65:35)(Figure 3 g). The elution of the oligomers in Figure 3 (g) is in the reverse order to SEC. Figure 3 is the typical examples for the combination of size exclusion and adsorption modes in the same column: size exclusion, a mixed mode of size exclusion and adsorption, and adsorption.

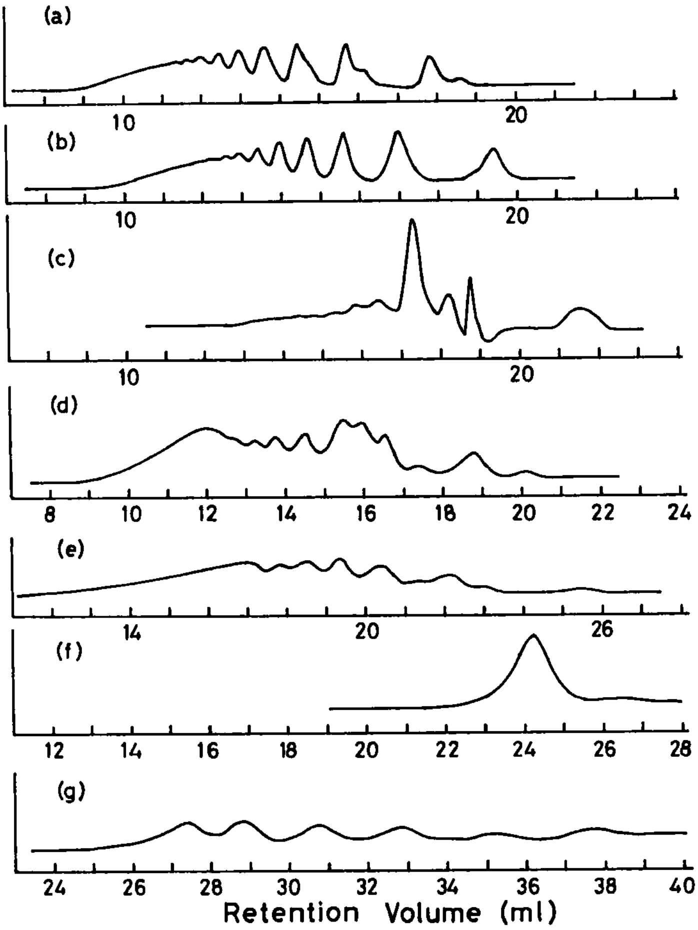

FIGURE 3. Chromatograms of epoxy resin prepolymer EPIKOTE 1001. Mobile phase: (a) THF, (b) THF-methanol (75:25), (c) (50:50), (d) THF-n-hexane (90:10), (e) (80:20), (f) (70:30), (g) (65:35). Attenuation: (a),(d) x0.64, (b), (c), (e), (f) x0.32, (g) x0.16

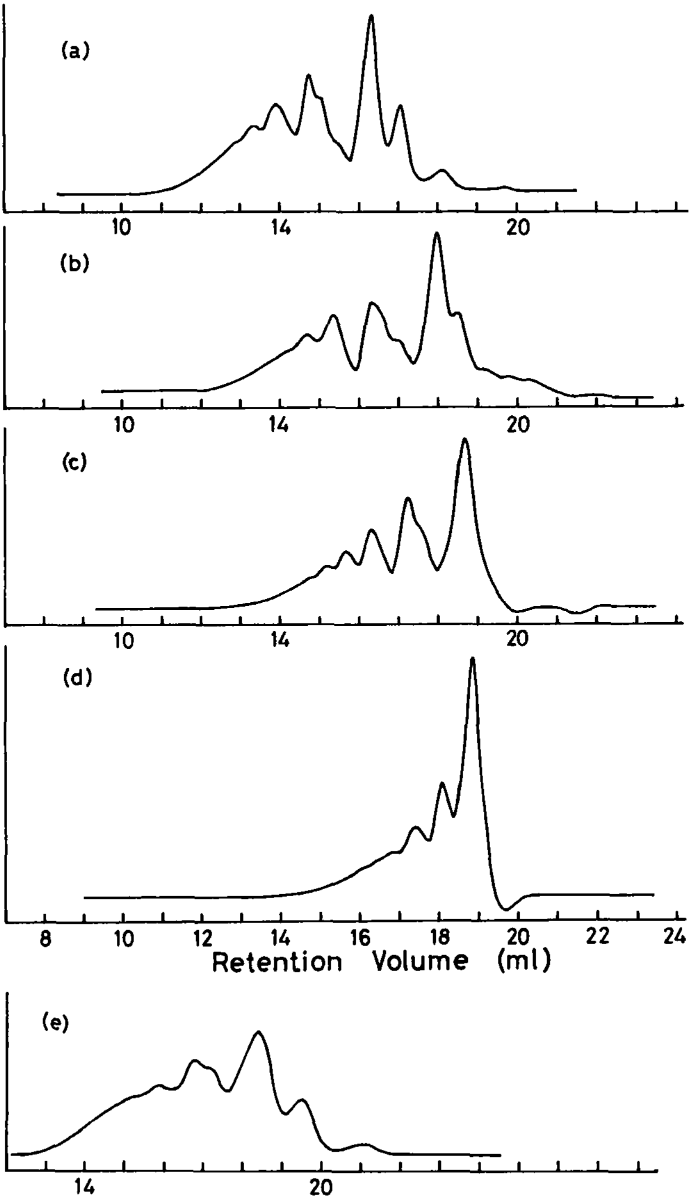

FIGURE 4. Chromatograms of methylated melamine-formaldehyde resin prepolymers. Mobile phase: (a) THF, (b) THF-methanol (75:25), (c) (50:50), (d) (25:75), (e) THF-n-hexane (90:10), (f) (80:20), (g) (70:30), (h) (60:40). Attenuation: (a) - (e), (h) x0.64, (f), (g) x0.32 AUFS.

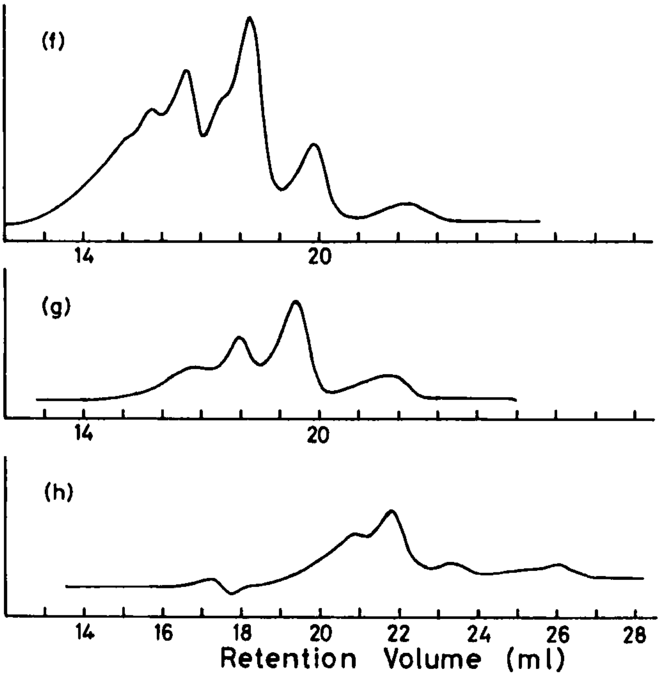

FIGURE 4. (Continued from the previous page.)

Figure 4 is the chromatograms for methylated melamine-formaldehyde resin prepolymers. Elution patterns similar to those in a PS gel-THF system were obained when the mobile phase was THF-methanol (50:50)(Figure 4 c) and (25:75)(Figure 4 d)[8]. Mononuclear melamine resin isomers appeared at retention volumes between 16 ml and 18.5 ml in the mobile phase of THF (Figure 4 a). Three peaks could be observed. Elution of these three peaks were in the reverse order to that in a PS gel-THF system[8].

The chromatograms of oligostyrene 600 (molecular weight 600) are shown in Figure 5. The addition of methanol retarded the elution of oligostyrenes and when the mobile phase was THF-methanol(75:25),all oligomers appeared at V_R = 19 ml as one peak.

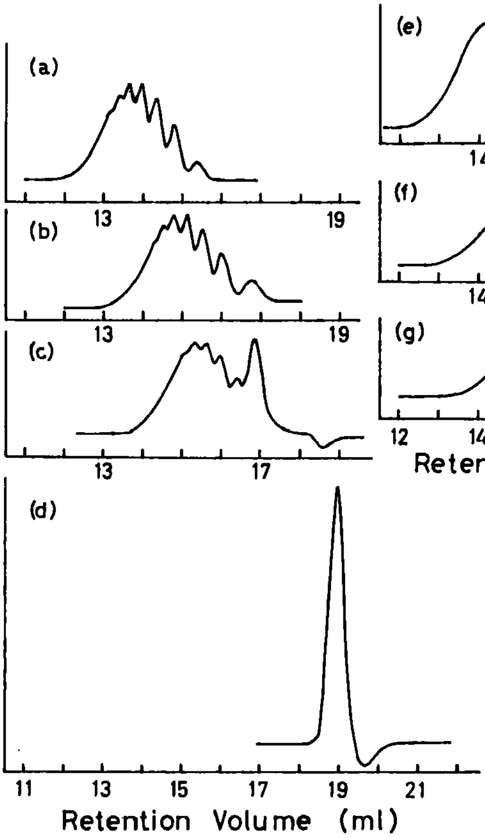

FIGURE 5. Chromatograms of oligostyrene 600. Mobile phase: (a) THF, (b) THF-methanol (75:25), (c) (50:50), (d) (25:75), (e) THF-n-hexane (90:10), (f) (80:20), (g) (70:30). Attenuation: (d), (e) x0.64, (a) - (c), (f), (g) x0.32 AUFS.

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REFERENCES

1. Mori, S., Identification and Determination of Phthalate Esters in River Water by High Performance Liquid Chromatography, J. Chromatogr., 129, 53, 1976.

2. Mori, S., Elution Behavior of Some Solutes on a Porous Polystyrene Gel in High Performance Liquid Chromatography, Anal. Chem., 50, 745, 1978.

3. Mori, S. and Yamakawa, A., Combination of Size Exclusion and Normal-Phase Partition Modes in High Performance Liquid Chromatography, Anal. Chem., 51, 382, 1979.

4. Hirata, N., Kasai, M., Yanagihara, Y., and Noguchi, K., Amphipathic Character of Hydrophilic Polymer Gel Columns, J. Chromatogr., 396, 115, 1987.

5. Mori, S., Interchangeable Use of Aqueous and Organic Solvents in a Hydrophilic Poly(vinyl Alcohol) Gel Column, J. Chromatogr., 452, 137, 1988.

6. Mori, S., Elution Behavior of Oligomers on a Polyvinyl Alcohol Gel Column with Chloroform, Methanol, and Their Mixtures, J. Liq. Chromatogr., 11, 1205, 1988.

7. Mori, S. and Uno, Y., Operational Variables for the Separation of Styrene-Methyl Methacrylate Copolymers According to Chemical Composition by Liquid Adsorption Chromatography, Anal. Chem., 59, 90, 1987.

8. Mori, S., Semimicro Size Exclusion Chromatography for Oligomers. II. Separation of Oligomers and Comparison with Conventional Columns, J. Liq. Chromatogr., 9, 1329, 1986.