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GEL PERMEATION CHROMATOGRAPHY OF THE CYCLIC MONOMERS AND OLIGOMERS IN NYLON 6 AND NYLON 66

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SUMMARY

The cyclic monomers and oligomers in nylon 6 and nylon 66 were separated and determined by gel permeation chromatography. The gels used in the experiment were Sephadex G-15, G-25 and Bio-Gel P-4. The ethanol extracts of nylon 6 and nylon 66 were dissolved in 0.1 *N* hydrochloric acid which was used as an eluant. The effluent was introduced into a flow cell and the absorbance at 210 mμ was measured continuously by means of a spectrophotometer. The method is applicable to 1–5 mg samples or less and the time needed for chromatography is less than 6 h. The presence of linear oligomers does not affect the determination of the cyclic oligomers.

Linear relationships between log M and several elution values, *viz.* V_e, V_e/V_t, V_e/V_0, K_d, and $V_e/(V_0 + V_t)$, have been confirmed for the cyclic monomer and oligomers of nylon 6. Deviation from linearity of the elution values of the cyclic dimer of nylon 66 implies that the dimension of the dimer is contracted in a solution compared with others.

INTRODUCTION

In most polyamides, cyclic monomers (*e.g.*, caprolactam for nylon 6), cyclic oligomers (cyclic dimer, trimer, etc.) and linear monomers and oligomers were considered to be the equilibrium products of polymerization. In numerous publications regarding the estimation of the monomer and oligomer in nylon 6, methods, often involving special techniques, for their determination have generally been based on weight differences.

ONGEMACH *et al.* determined the caprolactam (monomer) content in aqueous extracts of nylon 6 by gas chromatography[1] and the oligomer content, with that of the monomer[2], by differential refractometry and IR spectroscopy. According to BUKAČ *et al.*[3], the cyclic oligomer content could be estimated from the difference between percentage of the aqueous extracts and that of the monomer obtained by UV

and IR spectrophotometry. ANTON[4] directly determined the cyclic oligomer content in an aqueous extract of nylon 6 by IR spectrophotometry. By these methods it has not been possible to differentiate each cyclic oligomer (cyclic dimer, trimer, etc.) from the cyclic oligomer mixture in the sample.

Fractional sublimation[5] was applied for the differentiation and quantitative determination of the cyclic dimer to tetramer of nylon 6. Paper chromatography was also employed for differentiating the cyclic oligomers in nylon 6 (ref. 6) and nylon 66 (ref. 7). The cyclic oligomers separated on the paper chromatogram were determined colorimetrically at 420 mμ after color development of the spots by means of chlorine gas and *o*-tolidine/potassium iodide solution[6,8,9]. There is little information in the literature on the quantitative determination of the individual oligomers except these two methods (fractional sublimation and paper chromatography), which are lengthy, complicated and time-consuming.

The technique of gel permeation chromatography (GPC) has proved to be a versatile tool for the fractionation of a homologous series of macromolecules according to molecular size[10]. This technique is applicable to oligomer separation. Low-molecular-weight homologs in poly(ethylene glycol) were separated by GPC using cross-linked dextran gels (Sephadex)[11,12]. KUSCH AND ZAHN[13] isolated the higher oligoamides in several polyamides on a preparative scale by gel filtration of the polyamide extracts on Sephadex G-25 and Bio-Gel P-10. By their method, the extracts were dissolved in 30–50% acetic acid and loaded onto a column of gels (4 cm in diameter, 500 cm long). DETERMANN *et al.*[14] prepared a copolymer of methyl methacrylate and ethylene glycol dimethacrylate that was used for fractionation of low-molecular-weight polystyrenes. HEITZ *et al.*[15] fractionated oligophenylenes and oligourethanes using several cross-linked gels. The use of particular dextran gels for separations according to size was introduced by PORATH AND FLODIN[16].

The method described in this paper enables quantitative separation of the cyclic monomers and oligomers in nylon 6 and nylon 66. The ethanol extracts of nylon 6 and nylon 66 were dissolved in 0.1 *N* HCl, separated into fractions by GPC and then detected by UV spectrophotometry. The gels used in this study were the commercially available, cross-linked dextrans Sephadex (Pharmacia, Uppsala, Sweden) and the cross-linked polyacrylamide Bio-Gel (Bio-Rad Laboratories, Calif., U.S.A.).

EXPERIMENTAL

Materials

The gels used were Sephadex G-25 Fine (particle size, 20–80 μ), G-15 (40–120 μ) and Bio-Gel P-4 (200–400 mesh). These gels were used without further screening. Their regain in water was determined experimentally in our laboratory. The eluant was 0.1 *N* HCl in water; its pH was approx. 1.1. Cyclic oligoamides of nylon 6 and cyclic mono- and oligoamides of nylon 66 were obtained by evaporating the corresponding ethanol extracts. The cyclic dimer and trimer of nylon 6 were obtained from the oligomer mixture by fractional sublimation in accordance with the method of HEIKENS[5]. The cyclic monomer of nylon 66 was extracted with aceton from the oligomer mixture.

Packing

The dry gels were suspended in 0.1 *N* HCl and left overnight. The columns used were cylindrical glass tubes 15.6 mm in diameter and 100 (and 150) cm in length. The bottom ends were connected to 3-cm-long capillaries with a 2-mm bore by means of silicone rubber stoppers. Before packing, the columns were mounted vertically, and small pieces of glass wool were laid over the outlet capillaries. The swollen gels were then packed into the columns by the method of WIDÉN AND ERIKSSON[17]. After the packing, the columns were percolated overnight with the eluant to be used to stabilize the beds and to remove the dissolved materials in the gels. The tops of the column tubes were connected to 1-l Mariotte bottles through polyvinylchloride tubes inserted through silicone rubber stoppers.

Elution

A 5–30 mg portion of the cyclic mono- and oligoamides was weighed into a 10-ml flask and the flask was filled with 0.1 *N* HCl. If necessary the solution in the flask was heated in a water bath at 80°. Application of the sample solution was carried out by the method of FLODIN[18]. A 1-ml portion of the sample solution was introduced onto the column. A constant flow rate was regulated by means of the Mariotte bottle; the flow rate was kept at 30 ml/h for the Sephadex columns and 20 ml/h for the Bio-Gel column. Elution was carried out at constant temperature, and the volume of the eluates was checked by means of a graduated cylinder. Blue Dextran 2000 (Pharmacia) was applied to determine the void volume (V_0) of the columns and to check the homogeneity of packing.

Detection

A Hitachi double-beam grating spectrophotometer Model 124 equipped with a flow cell was used. The bottom end of the column tube was connected to the flow cell through a teflon tube. Cyclic mono- and oligoamides appearing in the effluent were determined by measuring the absorption at 210 mμ. A Hitachi QPD_{34} recorder was used for the continuous recording of the absorption at 210 mμ. Blue Dextran 2000 was determined at 620 mμ.

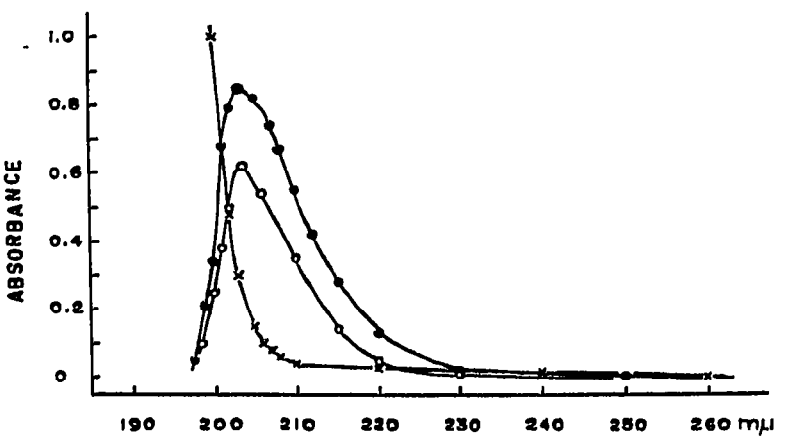

Fig. 1. UV absorption spectra for caprolactam and the cyclic dimer of nylon 6. Cell length: 1 cm. Reference side: for caprolactam and dimer, 0.1 *N* HCl; for 0.1 *N* HCl, H_2O. ●, Caprolactam, 0.0015% in 0.1 *N* HCl; ○, dimer, 0.005% in 0.1 *N* HCl; ×, 0.1 *N* HCl.

RESULTS AND DISCUSSION

The UV absorption spectra of the cyclic monomer and dimer of nylon 6 in 0.1 *N* HCl are shown in Fig. 1. The molar absorption coefficients (ε) of each cyclic monomer and oligomer at 210 mμ and 215 mμ were measured and listed in Table I. In computing the molar absorption coefficient, the assumption has been made that one mole of each oligomer is 113 g, considering that the absorbance in this region

TABLE I

THE MOLAR ABSORPTION COEFFICIENTS OF EACH CYCLIC MONOMER AND OLIGOMER

Monomer and oligomer	*Molar absorption coefficient, ε (l/mole[a]·cm)*		
	At 210 mμ	*Correction factor*	*At 215 mμ*
Nylon 6 monomer	2800	0.35	1470
dimer	980	1	390
trimer	970	1	460
tetramer	970	1	440
Nylon 66 monomer	1810	0.69	870
dimer and trimer (mixture)	1250	1	490
ε-Aminocaproic acid	68		55

[a] As $-(CH_2)_5CONH-$ unit (for nylon 66, half of the $-CO(CH_2)_4CONH-(CH_2)_6NH-$ unit is considered).

would be proportional to the quantity of the amide linkage. From the UV spectra, 210 mμ was selected for the detection of the monomer and oligomers. The value obtained by multiplying the absorbance of the monomer by the correction factor in Table I gives the impression that the ratios of absorbances of each monomer and oligomer represent their weight ratios.

The elution curves of the cyclic monomer and oligomer of nylon 6 and nylon 66 on G-15, G-25 and P-4 are shown in Fig. 2. Even though there was some overlap in elution peaks, the separation seems to be sufficient for the purpose of quantitative analysis. The variations in particle size and flow rate proved to be the most important factors for the efficiency of the column[18]. Better column efficiency can be obtained by using a small particle size. On Sephadex G-25 Superfine a better separation between the two adjacent peaks was obtained than on Sephadex G-25 Fine, but the time required for one cycle was longer because of the lower flow rate. Lengthening the gel head in the column also improved the separation, and at the same time a broadening of the peak width occurred.

The volume of sample solution injected governs the peak width[18]. A series of solutions ranging from 3 to 20 mg of the cyclic dimer of nylon 6 per 10 ml of 0.1 *N* HCl was prepared, and 1 ml of each solution was injected onto the column. The width of the elution peak at the base remained constant regardless of the weight of the dimer injected. This result implies that the apparent separability between the two adjacent peaks would improve when the sample concentration in the solution was

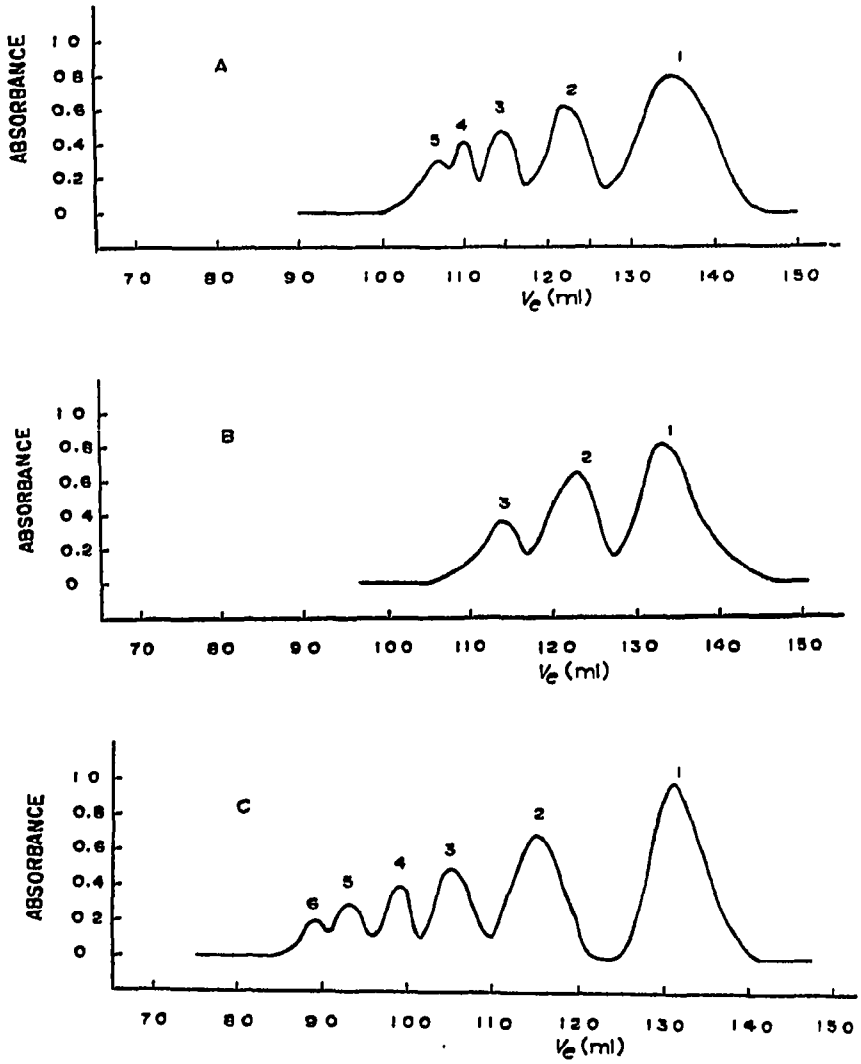

Fig. 2. Elution chromatograms of the cyclic monomers and oligomers of nylon 6 and nylon 66. (A) Separation of monomer and oligomers in nylon 6 on G-15 (column 15A). Concentration: 5 mg/ml. (B) Separation of monomer and oligomers in nylon 66 on G-25 (column 25A). Concentration: 4 mg/ml. (C) Separation of monomer and oligomers in nylon 6 on P-4 (column P4). Concentration: 3.5 mg/ml. 1 = cyclic monomer; 2 = cyclic dimer; 3 = cyclic trimer; 4 = cyclic tetramer; 5 = cyclic pentamer, 6 = cyclic hexamer.

increased in an appropriate range. This conclusion was verified by the experiments.

The column constants showing the column performance for Sephadex G-15, G-25 and Bio-Gel P-4 are listed in Table II. V_0 was experimentally determined as the elution volume for Blue Dextran 2000 (mol. wt. 2,000,000). V_t was calculated from the water regain (W_r), and the dry weight of gels *(a)*: $V_t = a \cdot W_r$. W_r was determined by centrifuging the swollen gels and by weighing the centrifuged swollen gels before and after drying.

The volume in a teflon tube between the bottom end of the column and the inlet of the flow cell was subtracted from the apparent elution volume. The corrected elution volumes *(V_e)* of each monomer and oligomer are presented in Table III. The

TABLE II

COLUMN CONSTANTS

Column symbol	15A	15B	25A	25B	P4
Type of gel	G-15	G-15	G-25	G-25	P-4
Column head (cm)	89.6	149	91	147	87
Dry weight of gel, a (g)	54	90	36.2	58.6	40
Total volume of gel bed, V_t (ml)	171	286	174	281	166
Void volume, V_0 (ml)	67	111[a]	69	112[a]	52
Inner volume, V_i (ml)	70	117[a]	83	133[a]	80
Volume of gel phase, V_x (ml)	104	175[a]	105	169[a]	114
Volume of gel matrix, V_g (ml)	34	58	22	36	34
Water regain, W_r (g/g of dry gel)	1.3		2.3		2.0
Bed volume per g dry gel (ml)	3.2		4.8		4.2

[a] Calculated in proportion to V_t of 15A and 15B, 25A and 25B.

TABLE III

THE ELUTION VOLUMES, V_e (ml), OF CYCLIC MONOMERS AND OLIGOMERS

Oligomer		*Type of gel/column symbol*					
		G-15/15A	*G-15/15B*	*G-25/25A*	*G-25/25B*	*P-4/P4*	*Mol. wt.*
Nylon 6	monomer	135	234	144	243	131	113
	dimer	122	211	133	223	115	226
	trimer	115	192	125	210	105	339
	tetramer	110	180	120	201	99	452
	pentamer	107	172	117	193	93	565
	hexamer					89	678
Nylon 66	monomer	122		133	222	117	226
	dimer	114		123	205	104	452
	trimer	104		114	190	90	678
ε-Aminocaproic acid				131			

TABLE IV

PER CENT OF CYCLIC MONOMERS AND OLIGOMERS IN THE ETHANOL EXTRACTS AND IN POLYMERS[a]

Oligomer	*Nylon 6*		*Nylon 66*	
	In extract	*In polymer*	*In extract*	*In polymer*
Monomer	82.5	8.70	42.3	0 67
Dimer	7.1	0.75	43.0	0.68
Trimer	4.5	0.47	14 7	0.23
Tetramer	2 8	0.30		
Pentamer	1.6	0.17		
Hexamer[b]	1.5	0.16		

[a] Nylon 6 and nylon 66 were prepared at the laboratory.
[b] Included oligomers larger than hexamer.

elution volume of ε-aminocaproic acid (ACA), which appeared in nylon 6 as a linear monomer, is near that of the cyclic dimer of nylon 6. However, the quantity of ACA is less than 0.1% (ref. 19) and in addition the molar absorption coefficient of ACA is small (Table I), so that the presence of ACA does not affect the determination of the cyclic dimer.

The cyclic monomer and oligomer mixtures in nylon 6 and nylon 66 were obtained by extracting nylon 6 and nylon 66 with ethanol for 24 h followed by evaporation of the ethanol. From the elution chromatograms of these mixtures, peak areas (= absorbance × ml) were calculated and the peak area of the monomer was corrected by multiplying the peak area by the correction factor given in Table I. The ratios of each peak area to the total peak area show the ratios of the monomer and individual oligomers in the mixture by weight. The monomer and oligomer contents in the polymer were also calculated on the basis of the weight of the extracts. The results are shown in Table IV. Accuracy and precision data are listed in Table V. In conclusion, it has been shown that with relatively simple equipment and the GPC technique, the presence of as little as 0.1% cyclic oligomers can be detected in nylon 6 and nylon 66.

Several authors have investigated the correlation between molecular weight and elution behavior. For example, linear proportionality between V_e/V_x and log M (ref. 20), V_e/V_0 and log M (refs. 21 and 22), and V_e and log M (ref. 23) was observed. DETERMANN AND MICHEL[24] investigated these relations systematically and proposed the following equation:

$$\log M = \log M_0 - (6.062 - 5.00d)\ (V_e/V_0)$$

In the course of our experiments several relationships were compared: molecular weight or logarithm of molecular weight were plotted against V_e, V_e/V_t, V_e/V_0, K_d, or $V_e/(V_0 + V_t)$. Linear relationships between log M and these elution values have been confirmed within experimental error for the monomer and oligomers of nylon 6 and between molecular weight and these elution values for nylon 66. Some examples for these relations are drawn in Fig. 3. Assuming linearity up to the upper limit, one should be able to calculate the exclusion limits of different gels. The exclusion limits for the cyclic oligomer of nylon 6 fall somewhere between 4600 and 5500 (G-15), 7300 and 9500 (G-25), and 3000 and 3400 (P-4). These limits vary with the elution functions.

TABLE V

RECOVERY EXPERIMENT OF THE CYCLIC MONOMER AND OLIGOMERS OF NYLON 6

Material	*Added (%)*	*Found (%)*	*Relative error (%)*
Monomer	20.7	22.3	+ 7.7
Dimer	39.5	36.9	− 6.6
Trimer	39.8	40.8	+ 2.5
Monomer	20.2	17.5	−13.4
Dimer	39.8	38.7	− 2.8
Trimer	40.0	43.8	+ 9.5

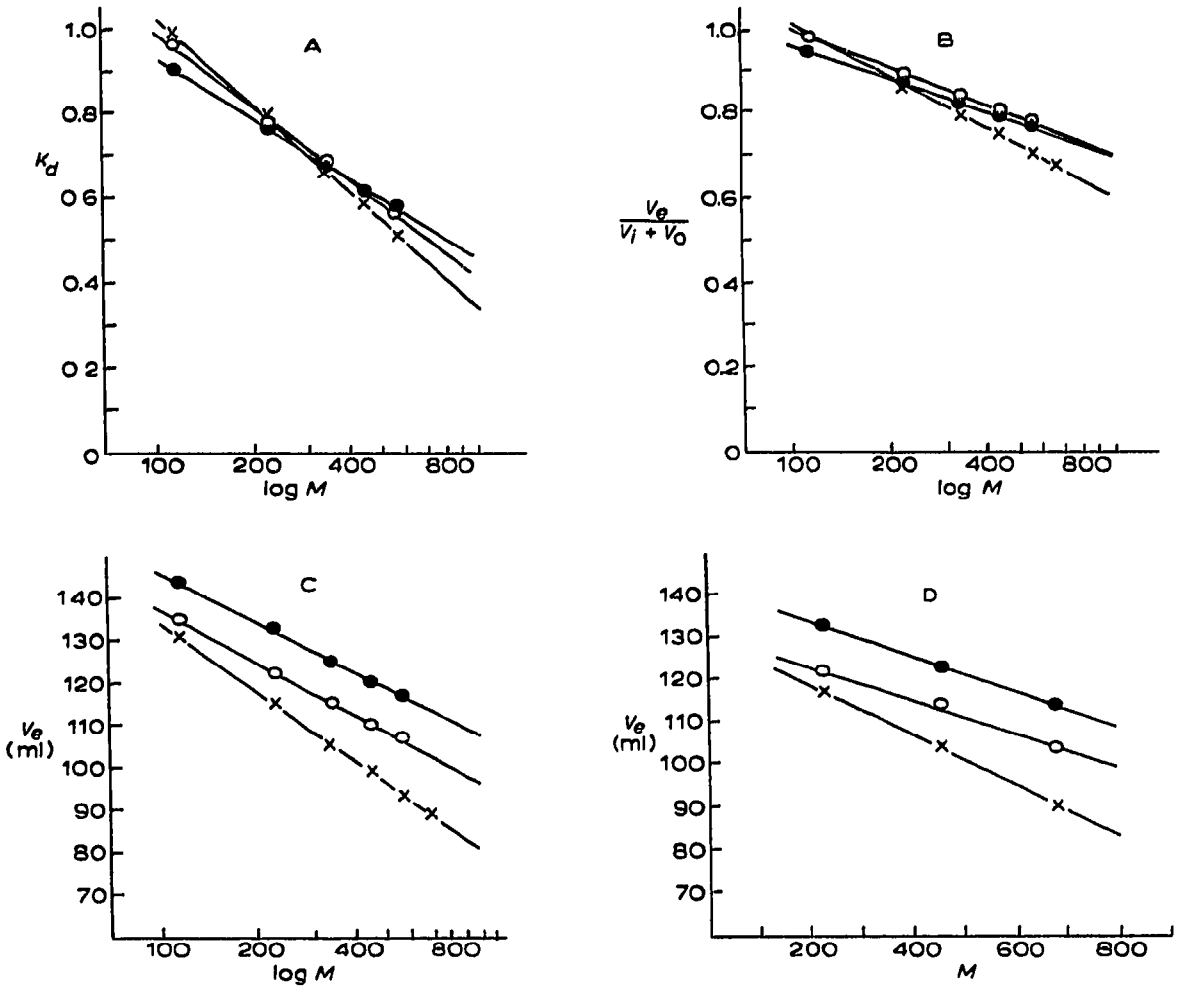

Fig. 3. Correlations between the elution volumes and molecular weights of cyclic monomers and oligomers on G-15 (column 15A), G-25 (column 25A), and P-4 (column P_4) (A) K_d *vs.* log M for nylon 6 monomer and oligomers. (B) $V_e/(V_i + V_0)$ *vs.* log M for nylon 6 monomer and oligomers. (C) V_e *vs.* log M for nylon 6 monomers and oligomers. (D) V_e *vs* M for nylon 66 monomer and oligomers. ●, G-25; ○, G-15; ×, P-4.

SIEGEL AND MONTY[25] stated that it is not the molecular weight, but the Stoke radius which governs the elution position in some special cases. The cyclic dimer of nylon 66 seems to correspond to this special case. The elution volumes for the cyclic monomer and trimer of nylon 66 are nearly coincident with those for the cyclic dimer and hexamer of nylon 6, which have the same molecular weights. The cyclic dimer of nylon 66 seems to have a higher elution volume than what can be expected from its molecular weight in comparison with the cyclic tetramer of nylon 6. This implies that the dimension of the cyclic dimer of nylon 66 is contracted in a solution compared with others.

The volume available for a solute in the gel phase was determined from the elution volume, the void volume and the inner volume of the gel column. From this point of view, the term of $V_e/(V_0 + V_t)$ is newly introduced in order to predict the elution behavior. The values of $V_e/(V_0 + V_t)$ of the same oligomer on Sephadex G-15

and G-25 columns are almost identical and so are the values of K_d. This function thus seems to be appropriate along with K_d. However, this is an empirical result and it is not certain whether this is an equation of universal validity, since the experiments were only done with one kind of sample and two types of gels in our laboratory. Further systematic investigation will be needed in this respect.

It is well-known that in aqueous solutions aromatic substances are retarded on Sephadex gels of the G-series[26]. This effect is particularly noticed in the highly cross-linked gels of G-10, 15 and 25. During our experiments, water was used as the eluant at first and the retardation effect was observed, especially in caprolactam. The separation between two adjacent peaks was very poor. Using 0.1 *N* HCl as the eluant, the retardation effect became far less pronounced and the solubility of the oligomers was also greatly improved.

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