

Correlations of Hydrodynamic Characteristics of Macromolecules and Their Retention Volumes in GPC

RESULT AND DISCUSSION

The exclusion liquid chromatography of polymers is a method of molecular hydrodynamics in which the separation of macromolecules according to size occurs in the absence of adsorption interaction of the polymer with the stationary phase. In this case the distribution coefficient K_d is the function of the ratio of hydrodynamic radius of the macromolecules (r) to the effective pore radius (a), and in a certain range of the r/a ratio the dependence $K_d = f(\log r/a)$ is linear.¹ This dependence is reflected in the well-known Benoit universal calibration curve²

$$\log([\eta]M) = C_1 + C_2 V_R \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, V_R is the retention volume of the fraction, and C_1 and C_2 are the constants characterizing the columns. Only one hydrodynamic characteristic is generally used $[\eta]$.

In the present communication poly(vinyl pyrrolidone) (PVP) and polyethylene glycol (PEG) were used as examples of the comparison of a more complete set of hydrodynamic characteristics with the retention volume (retention time) of fractions (samples). These characteristics are the translational diffusion coefficient D_0 , the coefficient of velocity sedimentation s_0 , and the concentration coefficient of sedimentation k_s .

The samples and fractions of PVP have been investigated by the authors previously.³ Moreover, PEG with different molecular weights (Serva Company) was investigated. A sodium acetate solution (0.1M) was used as solvent. Velocity sedimentation of PVP and PEG was investigated with a MOM-3170 analytical centrifuge (Hungary) in two-sector cells with formation of an artificial boundary. The height of the insert was 12 and 30 mm, which permitted the investigation of solution up to the concentration $c = 3 \times 10^{-4}$ g/cm³. For a number of samples, the concentration dependence of the sedimentation coefficient s obeying the equation $s^{-1} = s_0^{-1}[1 + (k_s + \bar{v})$

$\times c + \dots]$ was investigated, \bar{v} being the partial specific volume of the polymer in solution, which were determined pycnometrically.

Diffusion coefficients D were determined from the time dependencies of dispersion of the diffusion boundary formed in a glass cell at an average solution concentration of usually $c \sim 2.5 \times 10^{-4}$ g/cm³. The values of D obtained at these concentrations were taken for those of D_0 extrapolated to zero concentration. The optical system for recording the solution-solvent boundary in sedimentation-diffusion analysis was a polarizing interferometer.⁴

Viscometric measurements were carried out with an Ostwald viscometer. Chromatographic investigations were carried out on a Millipore Waters GPS II chromatograph with a refractometric detector, and the chromatograms were processed on a Data Module (M 730). Columns of the Tojo Soda TSK Company, G.6000 PW and G.3000 PW, connected in series 600×7.5 mm each were used. The chromatograms were symmetric and unimodal (Fig. 1). The retention volume of fractions was determined from the chromatogram maximum. The molecular weight values (M_{sD}) were calculated with Svedberg's equation. The experimental data are given in Table I.

It is known that $D_0 = kT/f$, $s_0 = [(1 - \bar{v}\rho_0)/N_A](M/f)$, $[\eta] = \Phi(\bar{h}^2)^{3/2}/M$, $k_s = B(\bar{h}^2)^{3/2}/M$, where $f = P\eta_0(\bar{h}^2)^{1/2}$ is the friction coefficient, \bar{h}^2 is the mean-square end-to-end distance of polymer chain in solution, η_0 is viscosity of solvent, k is the Boltzmann constant, Φ , P , B are the hydrodynamic coefficient depending on contour length and length of the Kuhn segment and on intramolecular hydrodynamic interaction and the excluded-volume effects in nonideal solvents. If dependence (1) is obeyed, it may be expected that similar relationships are also valid for other hydrodynamic characteristics or their combinations that depend mainly on the chain size. In the general case, it may be written that

$$\log[f(\bar{h}^2)] = C_i + C_{i+1}V_R \quad (2)$$

where $f(\bar{h}^2) = D_0$ or $s_0[\eta]$ or s_0k_s or s_0M^{-1} or k_sM . Figure 2 shows the corresponding dependencies, and Table II gives the parameters of straight lines plotted by the least-squares method.

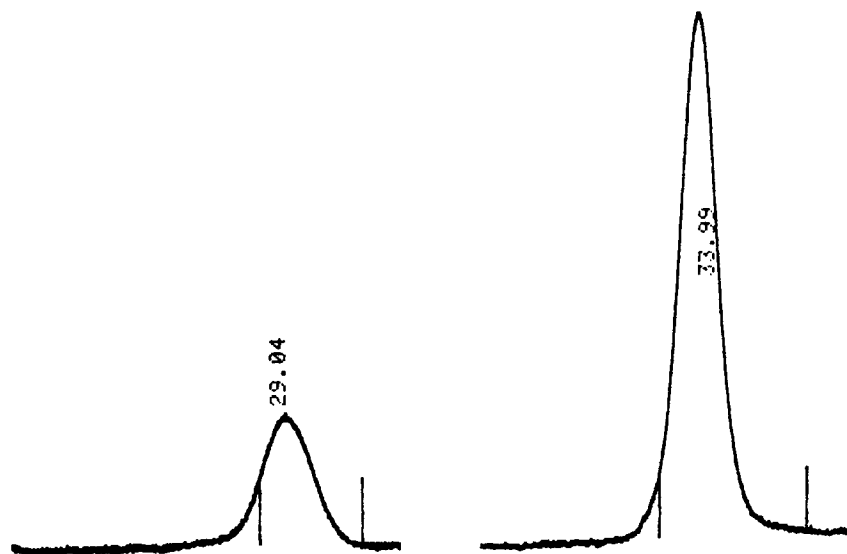


Figure 1 Chromatograms of samples of (a) poly(vinyl pyrrolidone) and (b) polyethylene glycol. The numbers are the values of V_R . The rate was 1 mL/mm at room temperature and a pressure of 10–20 atm. The sample concentration was $(0.5-1) \cdot 10^{-3}$ g/cm³, and the injected volume was 150–250 mL.

The parameters of equations of type (2) can be inter-related in pairs. Thus, if, e.g., $\log D_0 = C_9 + C_{10}V_R$ is compared with Eq. (1), then $C_{10} = (-\frac{1}{3})C_2$, and if this equation is rigorously correct, C_1 and C_9 are related to each other via the hydrodynamic invariant β or A_0^4 viz $\log(A_0T/\eta_0) = (C_1/3) + C_9$, where $A_0 = \beta k = R\eta_0(1 - \nu\rho_0)^{-1}M^{-2/3}$

$s_0[\eta]^{1/3} = (\eta_0 D_0/T)(M[\eta])^{1/3}$.⁴ When the dependencies containing s_0 and k_s are compared, it is necessary to introduce into consideration the sedimentation parameter β_s^5 .

Hence, the properties of the universal calibration dependence will be satisfied if the retention volume is com-

Table I Molecular Weight from s_0 and D_0

No.	$M_{sD} \cdot 10^{-3}$	$[\eta]$ (cm ³ /g)	$s_0 \cdot 10^{13}$ (s)	k_s (cm ³ /g)	$D_0 \cdot 10^7$ (cm ² /s)	V_R (cm ³)
1	2290	380	11.2	625	0.55	26.23
2	1950	420	9.5	—	0.55	26.21
3	1200	295	7.5	435	0.70	27.06
4	625	163	6.1	—	1.1	28.05
5	430	130	4.6	—	1.2	29.04
6	360	114	4.5	—	—	28.71
7	174	65	3.55	150	2.3	30.52
8	160	62	3.4	120	2.4	30.85
9	152	64	3.5	—	2.6	30.85
10	129	52	3.2	120	2.8	31.18
11	497	425	3.2	570	0.94	27.88
12	413	270	3.0	610	1.05	28.54
13	27.4	50	0.75	—	4.5	32.83
14	14.3	38	0.50	—	5.2	33.99

^a According to Svedberg's equation M_{sD} , intrinsic viscosity $[\eta]$, sedimentation coefficient at zero concentration s_0 , concentration coefficient of sedimentation k_s , diffusion coefficient D_0 at $c = 0$ and retention volume V_R of poly(1-vinyl-2-pyrrolidone) (1–10) and polyethylene glycol (11–14) in 0.1 M sodium acetate solution at 25°C.

pared with any hydrodynamic value or their combination, which are determined by the size of the macromolecule. This concept widens the possibilities of applying the method of gel penetration chromatography in combination with other transport methods in the investigation of polymer homologs.

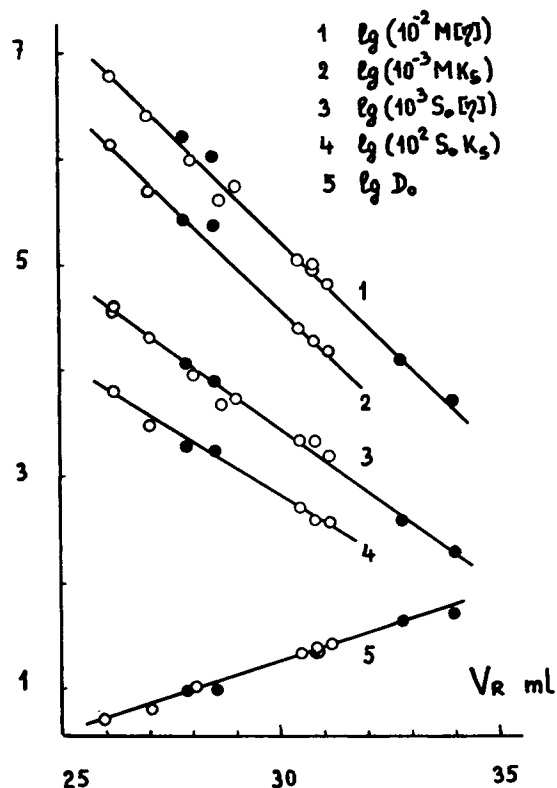


Figure 2 Dependences $\log(M[\eta])$ (1), $\log(Mk_s)$ (2), $\log(s_0[\eta])$ (3), $\log(s_0k_s)$ (4), $\log D_0$ (5) vs. retention volume V_R (open circles, PVP; filled circles, PEG).

Table II Correlations of Hydrodynamic Characteristics of Macromolecules and Their Retention Volumes

Characteristic	C_{i+1}	ΔC_{i+1}	C_i	r_i	n
$M[\eta]$	-0.414	0.012	19.745	0.9953	14
Mk_s	-0.395	0.019	19.491	0.9942	7
$s_0[\eta]$	-0.293	0.009	-1.730	0.9948	14
s_0k_s	-0.245	0.014	-2.809	0.9915	7
D_0	0.134	0.005	-10.759	0.9935	13

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