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Concentration Dependence of Coil Dimensions by Means of Exclusion Chromatography

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ABSTRACT: Decrease of the effective coil dimensions $\langle r^2 \rangle$ with increasing polymer volume fraction ϕ_2 has been measured by gel permeation chromatography for polystyrene standards ($2 < M \times 10^{-3} < 2500$) in toluene. Good correlation is found with the limiting equation $\langle r^2(\phi_2)\rangle / \langle r^2(0)\rangle \sim 1 - 0.043N^{0.72}\phi_2$ ($N >> 1$, $\phi_2 << 1$) based on computer simulation recently performed by De Vos and Bellemans.

The mode of the gel permeation chromatogram (PEV) is known to be shifted toward a larger elution volume when the concentration of injected solution is increased; the effect is more pronounced, the better the solvent, the higher the molecular weight of the sample or the narrower its molecular weight distribution.[1-7]

Many attempts have been made to isolate the various contributions to such a retardation behavior. Column overloading (secondary exclusion) and adsorption on the support may safely be ruled out. A viscosity effect, such as the so-called viscous fingering, cannot explain alone the mode dependency on concentration.[8] However, the observed trend might well be a consequence of the enhanced penetrability within the internal volume of the gel for the macromolecules whose effective dimensions in solution are a decreasing function of concentration.[9,10]

Recently, Janča et al.[11] made a thorough examination of the problem but failed to reconcile theory and experimental data on a quantitative basis. They assumed for the elution curves a Gaussian analytical form in conjunction with a linear calibration curve. However, the latter appears to be nonlinear in the interval considered by these authors, moreover, departure from a Gaussian profile, either symmetrical or asymmetrical, might also be a cause of the observed discrepancy.

The problem of the effective dimensions of the polymer molecule will be considered below in conjunction with some theoretical values computed by De Vos and Bellemans[12] for statistical coils in athermal solution.

Experimental Section

Procedure. A Waters Associates Chromatograph Model 200 has been equipped with five 4-ft Styragel columns (10^5, 10^5, 4×10^4, 10^4, 10^3) and operated at room temperature with toluene as eluent. Flow rate was kept at 1 mL/min; injection time interval was 120 s.

A water-jacketted syphon (volume = 2.41 mL) has been built to ensure better temperature control and to prevent solvent evaporation. Data were obtained in numercial form, by means of an analog/digital converter and of a serializer coupled to a chronoscope unit (Viscomatic, Fica), for further processing on a Hewlett-Packard 9830 A calculator. Fourier transform analysis has been applied to the elution curve to determine the mode position with a reliability of ±0.02 mL between two successive injections of the same elution. Solution concentration range was kept between 0.2 and 2.0 mg/g.

Average molecular weights of polystyrene standards purchased by Waters Associates (W) or Pressure Chemicals Inc. (PC) or synthetized in the laboratory (L) are given in Table I.

The calibration curve has been established at infinite dilution by appropriate extrapolation of the mode of the chromatograms, as discussed below. No corrections have been made for dispersion, assuming negligible influence of the latter on the concentration dependence of the mode.

Data given in Table I display the good fit of the results when a linear dependence is assumed for the mode of the elution curve vs. concentration of the injected solution. The error on the extrapolation eventually arising from this assumption amounts to less than 0.15 count for the PS2300 sample and becomes vanishingly small with decreasing molecular weight. The PEV increments refer to the situation prevailing at the top of the column set and will therefore be termed $[\Delta PEV/\Delta C]_{IN}$.

But on passage through the columns, the solution is continuously diluted. This will in turn cause the PEV values to be less shifted than expected solely on a molecular weight basis at equal injected concentration. The ratio of the peak height to the zeroth order moment of the chromatogram could be used as a rough estimate to calculate a relative dilution factor Q (Table I). In this way, one obtains the elution volume increments $[\Delta PEV/\Delta C]_{OUT}$ more appropriate to the conditions prevailing at the end of the column set. Accordingly, the proper average value should be comprised somewhere between the two limiting increments, i.e., $[\Delta PEV/\Delta C]_{IN}$ and $[\Delta PEV/\Delta C]_{OUT}$.

A linear relationship has also been assumed for the logarithm of the hydrodynamic volume V_h vs. concentration; this dependence has been calculated on a semiempirical basis proposed by Rudin,[9] using the eq

$$V_h = [\eta]M = 11.6 \times 10^{-3}\ M^{1.72} \qquad (1)$$

for the magnitude of V_h at infinite dilution.

Correlation of V_h with both PEV increments discussed above is given in Figure 1 and appears satisfactory in either case. Recently, the contraction of a N segment coil with increasing volume fraction of the polymer in an athermal solution has been evaluated by De Vos and Bellemans[12] in terms of the ratio of the

Table I
Linear Dependence of the Peak Elution Volume (PEV) (Counts) vs. Polymer Weight Fraction of Injected Solution

polymer	origin	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$(PEV)_{C\to O}$ (count)	$[\Delta PEV/\Delta C]_{IN}$ (count/%)	correlation	Q
PS2300	W	1990	2610	47.66	7.71	0.996	0.55
PS2025	W		2050	47.70	6.90	0.995	0.56
PS830	W	773	867	54.18	4.50	0.999	0.85
PS655	PC	640	670	55.47	3.14	0.969	0.71
PS451	W	404	498	57.11	1.80	0.963	0.82
PS370	PS	355	392	58.92	2.32	0.965	0.93
PS300	L	272	318	60.36	2.19	0.986	0.72
PS196	W	193	200	63.66	1.83	0.999	1.00
PS170	L	171	172	64.44	1.41	0.924	0.99
PS142	L	140	146	65.45	1.74	0.983	1.02
PS111	W-PC	111	111	66.58	1.34	0.996	1.09
PS67	L	67	71	70.28	1.19	0.997	1.02
PS55	L	55	59	71.72	0.90	0.931	1.02
PS34.5	W	36	33	73.94	0.74	0.977	1.10
PS20.5	W	20.2	20.8	77.54	0.37	0.969	1.16
PS9.8	W	9.6	10.5	81.25	0.40	0.783	1.01
PS3.55	W	3.1	4	86.09	0.25	0.850	1.17
PS2.1	W	1.95	2.1	88.25	0.30	0.814	1.10

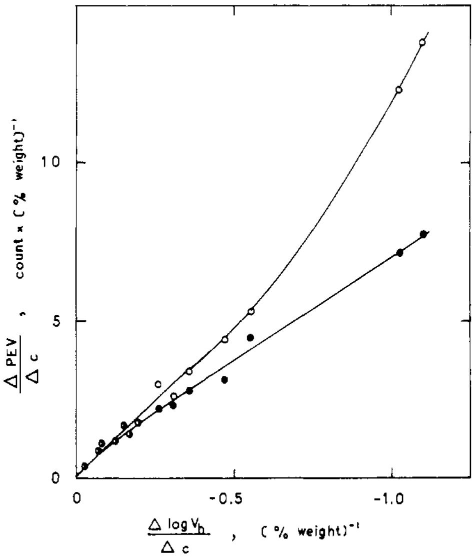

Figure 1. Mode increments $(\Delta PEV/\Delta C)_{IN}$ (●) or $(\Delta PEV/\Delta C)_{OUT}$ (○) vs. hydrodynamic volume increment $[\Delta \log V_h]/\Delta C$.

root-mean-square end-to-end distance computed at finite concentration $\langle r^2(\phi_2)\rangle$ and at infinite dilution $\langle r^2(0)\rangle$; the following relationship has been proposed

$$\langle r^2(\phi_2)\rangle / \langle r^2(0)\rangle \sim 1 - AN^{\alpha}\phi_2 \qquad (2)$$

with $A = 0.043$ and $\alpha = 0.72$.

Considering the well-established proportionality $\langle r^2\rangle \sim N^{1.20}$, together with $N = M/M_0$, where M_0 is the molecular weight of the monomer unit, the following expression is readily deduced

$$\langle r^2(\phi_2)\rangle / \langle r^2(0)\rangle = [M_{app}/M]^{1.20} \qquad (3)$$

M_{app} and M are the apparent and true average molecular weight, respectively, obtained by means of the same calibration curve, from PEV values taken at finite and vanishing concentration.

Rearrangement of eq 2 with eq 3 gives the expression

$$\log (1 - [M_{app}/M]^{1.20}) = \log A + \alpha \log N + \log \phi_2 = \text{constant} + \alpha \log M \quad (4)$$

Equation 4 has been plotted in Figure 2 with molecular weight values based on $[\Delta PEV/\Delta C]_{OUT}$. The curve assumes the predicted slope when M approaches infinity. The pronounced curvature at low molecular weight might be due to the inadequacy of eq 1 in the range of molecular weight discussed, although one should also bear in mind that the coil dimensions become altered by less than 1%. In the range of $M > 10^5$, the slope is 0.77. For the same plot, but resting on the $[\Delta PEV/\Delta C]_{IN}$ values, the slope is 0.58. In view of the approximations made dealing with the experimental data, and of the restrictions associated with the theoretical model assumed, correlation between predicted and experimental dependence appears to be satisfactory.

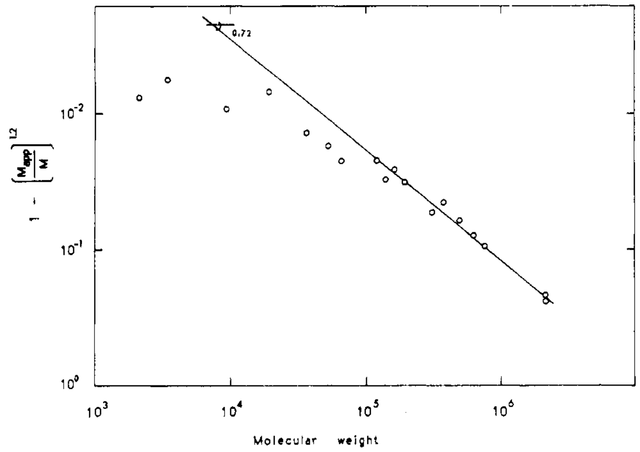

Figure 2. Relative coil contraction measured at finite volume fraction ϕ_2 vs. molecular weight (eq 4); (—) theoretical prediction by De Vos and Bellemans.[12]

However, the difficulties to relate the proper concentration to the PEV could be somewhat circumvented using the differential approach recently proposed by E. G. Bartick and J. F. Johnson.[14] In this case, the polymer concentration in the mobile phase can be set unambiguously at a known magnitude. In the same way, the occupation rate of the porous volume is also maintained unaltered but at a level depending on both column characteristics and molecular weight distribution of the polymer in the eluent. Consequently, the separation will not proceed at the same concentration constraints for high and low molecular weight species.

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