

Discussion on Gel Permeation Chromatography Calibration

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ABSTRACT:- Gel permeation chromatography (GPC) uses an eluent (mobile phase) and a porous gel that separates polymer molecules based on size or hydrodynamic volume. Smaller molecules spend more time in the pores, which increases retention time. A common eluent is tetrahydrofuran. GPC is used to determine relative molecular weights of polymers. Thus, the pore size of the gel is controlled. Grubisic, et al (1967) reasoned that the Einstein viscosity law, $[\eta] = K (V_e/M)$, could be employed to allow for a universal correlation. $[\eta]$ is the intrinsic viscosity, V_e is the hydrodynamic volume of the polymer, M is the molecular weight of the polymer and K is a constant. Flory (1953) says $K = 0.025 N_0$, where N_0 is Avogadro's number. We present the graph from Grubisic, et al as reproduced in Bovey/Winslow (1979) with comments and how this is useful for polymer science.

KEYWORDS:- “gel permeation chromatography” “hydrodynamic volume” “Einstein viscosity law”

I. INTRODUCTION

In order to understand gel permeation chromatography, GPC, it is necessary for the reader to know that the principle of corresponding states is involved here. For the universal calibration, Grubisic, et al used Einstein's viscosity relation, which is understood by Flory. GPC is used where porous beads let small molecular weight molecules in and keep the higher molecular weight polymer out. As the solution moves down the column, the high molecular weight polymer has a smaller retention time (volume) because it doesn't penetrate the pores as much.

Obviously, the pore size is varied to allow a range of molecular weight polymers to be distinguished. See Fig. 1, the Grubisic, et al curve for $[\eta] M$ vs retention volume to see that the curve is not linear. For Fig. 2, there is a curve from Guggenheim (1945) where small molecules have T/T_c vs ρ/ρ_c plotted. In Fig. 2 we see that it is also not linear. In both figures included here, each curve shows corresponding states. Grubisic, et al's curve is a calibration because any polymer with $[\eta] M$ from 10^5 to 10^9 is included: the numbers are single-valued. A polymer would be put into the column and its retention time is used to give the corresponding molecular weight given that the intrinsic viscosity $[\eta]$ is known. In the Discussion section, the author will discuss $[\eta]$ and how it is known.

II. RESULTS

Flory remarks on page 606 that one is unable to calculate V_e , the hydrodynamic volume, of the polymer. For Grubisic, et al,

$$K = 0.025 N_0 \quad (1)$$

which follows Einstein. For the Grubisic, et al graph, their plot of experimental data shows that the elution volume is a single-valued function where all of the points follow the same curve of $\log([\eta] M)$ vs elution volume irregardless of the polymer used.

One uses the same column, solvent and temperature, so it is universally calibrated and this is an experimental result. Einstein got, Flory page 606.

$$(\eta - \eta_0) / \eta_0 = 2.5 (n_2 / v) V_e \quad (2)$$

where n_2 is polymer molecules in the system, v is volume of the system and V_e is the hydrodynamic volume with η being the viscosity of the solution and η_0 the viscosity of the solvent.

III. DISCUSSION

Going further, Eq. (3) is from Flory page 606.

$$n_2 / v = (c N_0) / (100 M) \quad (3)$$

$$(\eta - \eta_0) / \eta_0 = \eta_r - 1 \quad (4)$$

where c = concentration in grams per 100 ml, N_0 is Avogadro's number and M is the molecular weight of the polymer.

Using (2), (3) and (4) we obtain,

$$\eta_r - 1 = (0.025 c N_0 V_e) / M \quad (5)$$

$$\lim_{c \rightarrow 0} ((\eta_r - 1) / c) \equiv [\eta] = (0.025 N_0 V_e) / M \quad (6)$$

And this gives Grubisic, et al, because V_e is independent of c .

$$[\eta] = (K V_e) / M \quad (7)$$

Then, we get (1). $[\eta]$ is the intrinsic viscosity measured by a viscometer and its units are deciliters per gram.

IV. CONCLUSIONS

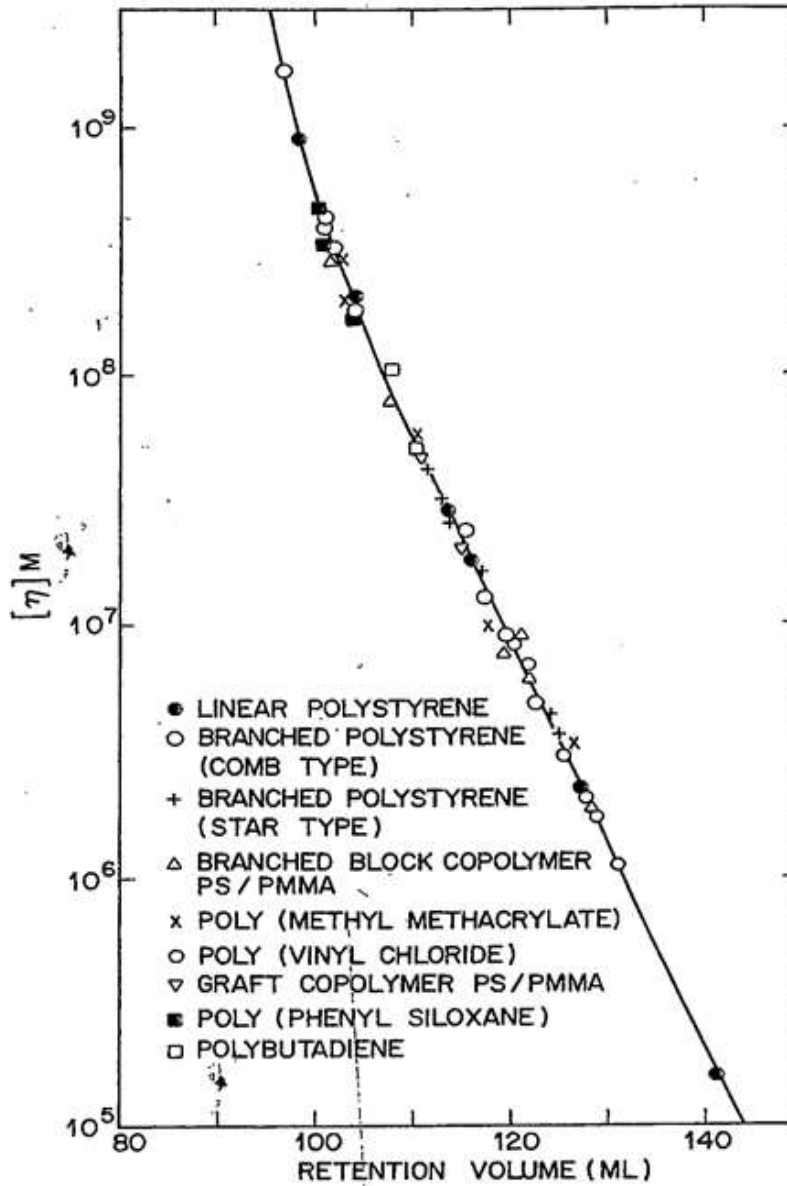
Grubisic, et al have come up with a way of calibrating gel permeation chromatography without having to calculate the hydrodynamic volume of the polymer, having shown a conclusive curve based on a theoretical formula by Einstein.

ACKNOWLEDGMENTS

Let me mention a long-term friend Joel Bresolin who has a keen interest in producing art. I am a collector of Joel's art with five of his works on my walls. Joel is a Catholic, as I am.

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Universal correlation between $[\eta]M$ and retention volume (Grubisic *et al.*, 1967).

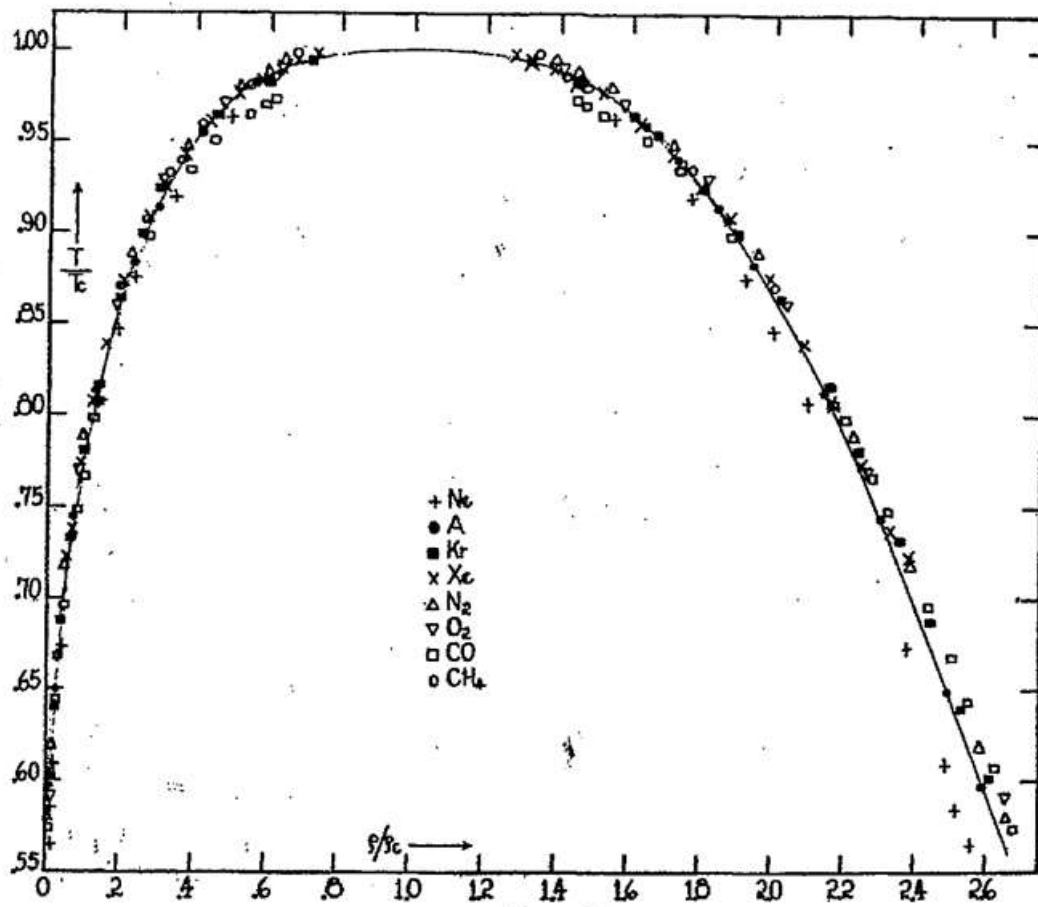


FIG. 2.

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