

## Solvent and Concentration Dependence of Hydrodynamic Volumes and GPC Elution Volumes

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### Synopsis

The sizes of dissolved polymers can be estimated a priori at infinite dilution and under theta conditions from existing theories. The effects of concentration can be calculated by assuming that the hydrodynamic volume decreases from a maximum value at infinite dilution toward the theta condition volume, which is reached when the volume fraction of solvated polymer in solution is unity. The predicted hydrodynamic volumes coincide with results of small-angle x-ray scattering and effects of solvent and concentration on gel permeation chromatography elution volumes.

### INTRODUCTION

A previous article from this laboratory has described a semiempirical model which could be used to calculate the effect of concentration on the effective volume of solvated polymer molecules and hence correct for concentration effects in gel permeation chromatography (GPC).<sup>1</sup> This model has also been applied to universal calibration in GPC.<sup>2</sup> The theory mentioned does not fit experimental observations in theta solvents, where GPC elution volume is essentially independent of polymer concentration.<sup>3</sup> This article describes a revised theory which is less empirical and which fits the elution behavior of polymers in all solvents in GPC.

A recent report by Hayashi and co-workers<sup>4</sup> gives results of direct measurements of the radius of gyration of a polystyrene in toluene. Our new model is shown here to predict the observed behavior quite well.

Any theory which is to be of practical use in this connection must be predictive, and we have therefore restricted our model to use of parameters which are readily available a priori, without recourse to experimental data which the model is intended to anticipate. In effect, this limits the input to the theory to the intrinsic viscosity (which can be obtained readily from a single measurement of relative viscosity in the particular solvent of interest<sup>5</sup>) and to application of certain universal relations which are known not to be exactly true in all circumstances. The data cited below show that this approach is practically useful, however, for predictions of polymer size as a function of solution concentration, despite any deficiencies in theoretical rigor.

## THEORY

We first estimate the dimensions of a polymer with given size in the unsolvated condition and dissolved at infinite dilution in the solvent of choice. These estimates are taken from the work of others and are repeated here in very brief form for the sake of clarity. The values obtained are then used to calculate the effects of concentration changes on the hydrodynamic volume of the polymer solute.

An equivalent hydrodynamic sphere model is used following Flory.<sup>6</sup> Under theta conditions the polymer is taken to be unswollen, and its intrinsic viscosity  $[\eta]_\theta$  is given by

$$[\eta]_\theta = K_\theta M^{0.5} \quad (1)$$

where  $M$  is the polymer molecular weight and  $K_\theta$  is assumed to be a universal constant which can be calculated with sufficient accuracy from the Flory-Fox<sup>7</sup> equation:

$$K_\theta = 2.5 \times 10^{-1} \frac{\beta^3}{M_0^{3/2}} \text{ (in cm}^3/\text{g)}. \quad (2)$$

In eq. (2),  $\beta$  (in Å) is an effective bond length typically equal to triple the carbon-carbon bond distance ( $\beta = 4.96$  Å for polystyrene<sup>8</sup>) and  $M_0$  is half the formula weight of the repeating unit in a vinyl polymer. For polystyrene, eq. (2) yields  $K_\theta = 8.135 \times 10^{-2}$  cm<sup>3</sup>/g in reasonably good agreement with experimental results.<sup>9</sup>

In any solvent, the intrinsic viscosity of the particular polymer is given by the Mark-Houwink equation with appropriate constants:

$$[\eta] = KM^a. \quad (3)$$

The radius of gyration of the solvated polymer at infinite dilution  $S_0$  follows from

$$[\eta] = \phi' \frac{S_0^3}{M} \quad (4)$$

according to several theories.<sup>10</sup>

Flory's value<sup>6</sup> of  $3.1 \times 10^{24}$  for  $\phi'$  (with  $[\eta]$  in cm<sup>3</sup>/g) is satisfactory for this application. Use of a solvent-dependent value<sup>11</sup> for  $\phi'$  would make the resulting mathematics more cumbersome. Dimensions calculated with the aid of Flory's universal constant are within experimental uncertainty of GPC data in any case, as we show below. The  $S_0$  values estimated from eq. (4) are in good agreement with results of direct measurements of polymer dimensions by neutron and light scattering.<sup>12</sup>

The hydrodynamic volume  $V$  of the solvated polymer is defined as

$$V \equiv v\epsilon \quad (5)$$

where  $v$  is the unswollen volume and  $\epsilon$  is a dimensionless swelling factor which is equal to  $\alpha^3$  in Flory's formalism.<sup>6</sup> The unswollen volume is evident that under theta conditions and in terms of the radius of gyration:

$$v = \frac{4\pi}{3} \frac{[\eta]_\theta M}{\phi'} = 0.338 \times 10^{-24} \frac{\beta^3 M^{1.5}}{M_0^{3/2}} \text{ (in cm}^3/\text{molecule)} \quad (6)$$

with  $\beta$  in Å. Similarly, the swelling factor at infinite dilution,  $\epsilon_0$ , is

$$\epsilon_0 = \frac{[\eta]}{[\eta]_0} = \frac{KM^{a-0.5}M_0^{3/2}}{0.25\beta^3}. \quad (7)$$

This reduces to unity under theta conditions since  $K$  is then given by eq. (2).

It now remains to calculate  $\epsilon$  as a function of concentration. It is well known that the dimensions of dissolved polymers decrease with concentration,<sup>13-17</sup> but no current theory seems to account quantitatively for the observed trends.<sup>4</sup> The following argument parallels that used with previous, less exact models used to account for this phenomenon.<sup>1,2</sup>

We assume that the range of the swelling factor  $\epsilon$  is such that  $\epsilon_0 \leq \epsilon \leq 1$ , where  $\epsilon_0$  characterizes the polymer at infinite dilution ( $c = 0$ ) and is given by the ratio  $v\epsilon_0/v$  or the equivalent formulation in eq. (7). The other limit to  $\epsilon$  occurs at a concentration  $c_x$ , which is assumed to correspond to a critical volume fraction  $\phi_x$  of polymer in solution at which the dimensions of the solvated macromolecules have been reduced to those prevailing under theta conditions ( $\epsilon = 1$ ).

We further assume that  $1/\epsilon$  and  $c$  are linearly related between the limits ( $\epsilon = \epsilon_0, c = 0$ ) and ( $\epsilon = 1, c = c_x$ ). This is the simplest possible expression for the inverse dependence of  $\epsilon$  on  $c$ . It is consistent with the limited available evidence<sup>17</sup> and produces results in accord with experiment, as shown below. This assumption leads to eq. (8) as an expression for  $\epsilon$  as a function of  $c$ :

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0} + \frac{c}{c_x} \left[ \frac{\epsilon_0 - 1}{\epsilon_0} \right]. \quad (8)$$

An a priori formulation of  $c_x$  is needed to render this equation useful. This can be obtained as follows from geometric considerations.

In general, the volume fraction  $\phi$  of solvated polymer at any concentration  $c$  (in g/cm<sup>3</sup>) is

$$\phi = \frac{N_0 c v \epsilon}{M} \quad (9)$$

where  $N_0$  is Avogadro's constant. The effective volume fraction at infinite dilution is obtained from

$$\lim_{c \rightarrow 0} \left( \frac{\phi}{c} \right) = \frac{N_0 v \epsilon_0}{M} \quad (10)$$

while the volume fraction  $\phi_x$  and corresponding concentration  $c_x$  of polymer when  $\epsilon$  has been reduced to unity are related by

$$\phi_x = \frac{N_0 c_x v}{M}. \quad (11)$$

From eq. (8), then,

$$\epsilon = \frac{M \phi_x \epsilon_0}{M \phi_x + N_0 v c (\epsilon_0 - 1)}. \quad (12)$$

Also, since, from eq. (4),

$$v = \frac{4\pi[\eta]_0 M}{3\phi'} \quad (13)$$

eq. (12) can be written as

$$\epsilon = \frac{3\phi' \phi_x \epsilon_0}{3\phi' \phi_x + N_0 c (\epsilon_0 - 1) 4\pi [\eta]_\theta} \quad (14)$$

and from eq. (7),

$$\epsilon = \frac{3\phi' \phi_x [\eta]}{[\eta]_\theta (3\phi' \phi_x + 4\pi N_0 c ([\eta] - [\eta]_\theta))} \quad (15)$$

The volume of a polymer molecule of concentration  $c$  is given by combining eqs. (13) and (15) as

$$v\epsilon = \frac{4\pi \phi_x [\eta] M}{3\phi' \phi_x + 4\pi N_0 c ([\eta] - [\eta]_\theta)} \quad (16)$$

Since  $\phi_x$  occurs in both the numerator and denominator of eqs. (14)–(16), the model will not be very sensitive to the exact value chosen for this parameter. We will proceed by taking  $\phi_x = 1$ . That is to say, the polymer molecules in solution are assumed to have shrunk to their theta condition dimensions when the available space is entirely filled with solvated polymer. It should be noted that the calculated dimensions in very dilute systems would not be changed much if we had taken  $\phi_x$  as low as 0.524, which is the occupied volume in cubic packing of uniform spheres.

With unit  $\phi_x$ , we have

$$\epsilon = \frac{9.3 \times 10^{24} [\eta]}{[\eta]_\theta (9.3 \times 10^{24} + 4\pi (6.022 \times 10^{23}) ([\eta] - [\eta]_\theta))} \quad (15a)$$

and

$$v\epsilon = \frac{4\pi [\eta] M}{9.3 \times 10^{24} + 4\pi (6.022 \times 10^{23}) c ([\eta] - [\eta]_\theta)} \quad (16a)$$

where the units of  $c$  and the intrinsic viscosities are in terms of g/cm<sup>3</sup>.

## RESULTS

Hayashi and co-workers have recently reported results of measurements of the dimensions of a 110,000 molecular weight polystyrene in concentrated solution in toluene at 25°C.<sup>4</sup>

For this sample, eqs. (1) and (2) yield  $[\eta]_\theta = 26.98$  cm<sup>3</sup>/g. The radius of gyration,  $S_0$ , under theta conditions is then estimated from eq. (4) to be 98.6 Å. This value is somewhat higher than the light-scattering measurements at 91.4 Å.<sup>18</sup> With the Mark-Houwink constants, eq. (3), given by Outer and co-workers,<sup>19</sup> the intrinsic viscosity of this polymer in toluene is 51.17 cm<sup>3</sup>/g, which results in a value of  $S$  equal to 124 Å. Light-scattering figures for this molecular weight are 119 Å<sup>18</sup> and 120 Å.<sup>20</sup> The infinite dilution swelling factor estimated from this model is thus equal to 1.9, compared to the experimental value of 2.2. This agreement is close enough for present applications.

The radii of gyration calculated from eq. (16a) at concentrations of 0.005 g/cm<sup>3</sup>, 0.031 g/cm<sup>3</sup>, and 0.061 g/cm<sup>3</sup> are 118 Å, 104 Å, and 98.6 Å, respectively. The latter value is equal to  $S_0$ , since  $c_x$ , eq. (11), equals 0.046 g/cm<sup>3</sup>. The corresponding experimental figures<sup>4</sup> from small-angle x-ray scattering are

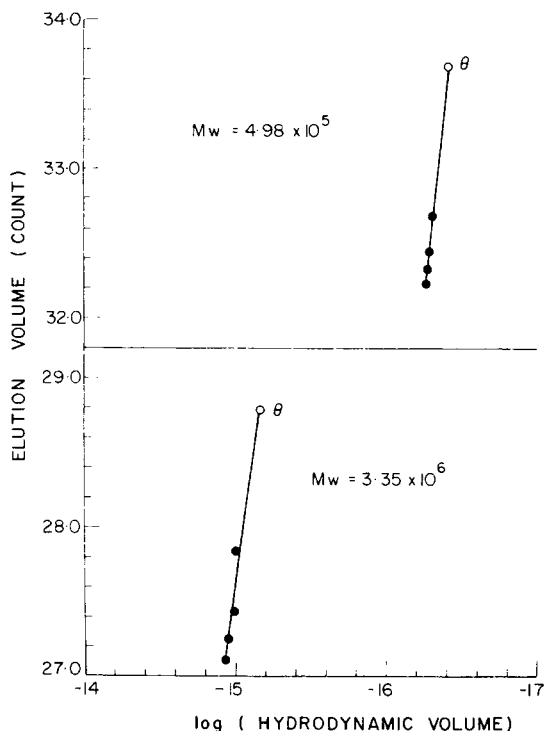


Fig. 1. Elution volumes of polystyrenes at different concentrations in butanone (●) and in butanone-methanol theta solvent mixture (○). Data from ref. 4.

119 Å, 101.5 Å, and 96.5 Å. The agreement is quite good, considering the absence of adjustable parameters in the model.

The model can be tested further against gel permeation chromatography results since this technique separates on the basis of hydrodynamic size and elution volumes obtained at different concentrations should therefore lie on a common line with a given column set.

Berek and co-workers<sup>3</sup> have pointed out that our previous model<sup>1,2</sup> does not fit GPC data in theta solvents. Their results, which were obtained with glass column packings, are not suitable for analysis in the present context because elution volumes in a good solvent are shown as higher than those in a theta solvent. This implies a lower hydrodynamic volume in the more concentrated good solvent solutions, and this seems to contradict general experience.

The GPC data of Kato and Hashimoto<sup>21</sup> have been analyzed according to our model. These include elution volumes through polystyrene gel columns of polystyrenes dissolved in butanone and in a theta solvent mixture of butanone and methanol. Hydrodynamic volumes were calculated from eq. (16a) using eqs. (1) and (2) for  $[\eta]_{\theta}$  and the Mark-Houwink coefficients of Oth and Desreux<sup>22</sup> for butanone solutions. Figure 1 records elution volumes and corresponding logarithms of calculated hydrodynamic volumes. All values lie on common curves (which are linear in this case) of elution volume against  $\log(v\epsilon)$ . The theta-condition hydrodynamic volumes are not strikingly different

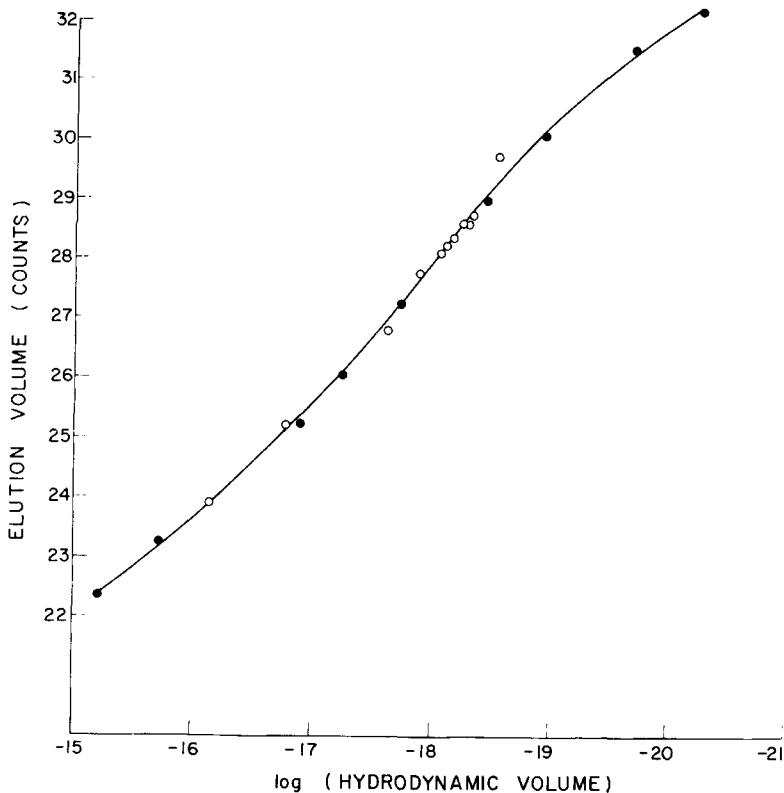


Fig. 2. Elution volumes of polystyrenes (●) at  $0.0025 \text{ g/cm}^3$  and poly(dimethylsiloxanes) (○) in *o*-dichlorobenzene at  $87^\circ\text{C}$  (ref. 23).

from those in butanone because the latter liquid is not a good solvent for polystyrene.

Figure 2 records the GPC elution volume data of Dawkins and Hemming<sup>23</sup> for two polymer types in *o*-dichlorobenzene at  $87^\circ\text{C}$ . This solvent is a good solvent for polystyrene and a theta solvent for poly(dimethylsiloxane). As shown, all data fall on a common curve of elution volume against log (hydrodynamic volume) as calculated with eq. (16a) and the Mark-Houwink constants given in the cited reference.<sup>23</sup>

## DISCUSSION

The examples quoted show that the theory provides useful predictions of the effects of concentration and solvent type on the effective hydrodynamic volumes of dissolved polymers. This does not necessarily mean that the theory is correct in all details, however. We have assumed an inverse relation between  $\epsilon$  and  $c$ , up to a limiting value of  $c$  corresponding to a critical volume fraction  $\phi_x$ . This concept seems to have merit, at least in a predictive sense. The choice of  $\phi_x$  is not critical, however, since any value which can be reasonably adduced from packing properties of uniform spheres will not affect the calculated hydrodynamic volumes very much.

The ability of the model to rationalize the effects of solvent and concentra-

tion on GPC data is important and useful. We are, however, not calculating the actual volume which a solvated polymer molecule presents to a porous gel. This volume must be many times larger than that estimated on the basis of the radius of gyration, although it seems reasonable that both volumes should change in a parallel fashion with varying experimental conditions.

At the present time, the only prudent claim for the theory given seems to be that it is useful. Further direct measurements of molecular size, such as those of Hayashi and co-workers,<sup>4</sup> are needed to determine how closely the calculated dimensions correspond in fact to those of real systems.

Application of the new model presented here to correction for concentration effects and universal calibration in gel permeation chromatography is essentially the same as that of the semiempirical procedure described in earlier articles,<sup>1,2</sup> except that the present theory accounts for observations in theta and poor solvents where the initial model was deficient.

Sample concentration effects may complicate the use of GPC to characterize the molecular weight distributions of polymers because peak elution volume may increase with increasing concentration of a given polymer in the feed to the GPC columns, whereas the calibration procedure assumes a unique relation between elution volume and molecular weight alone. The Benoit  $[\eta]M$  calibration method<sup>24</sup> is sound, provided the elution volumes of the fractions used for calibration are measured at infinite dilution. This is not generally convenient, or even possible, and the procedure thus benefits from modification by the theory presented here, which predicts the variation of effective hydrodynamic volume with concentration.

The model reported here produces GPC calibration results which differ from those estimated at infinite dilution only when the effects of rather small concentration changes result in marked variations in hydrodynamic volumes of solvated polymers. This occurs particularly with high molecular weight samples, narrow distribution polymers, and good solvents. Examples are given in reference 2. The procedure outlined here appears to be a more general method than the  $[\eta]M$  calibration, but it reduces to an equivalent form in less critical applications.<sup>2</sup>

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