Prediction of Osmotic Pressures of Polymer Solutions

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Synopsis

A theory which has been developed to account for the effects of concentration on the equivalent hydrodynamic volumes of dissolved polymers has been combined with a statistical mechanical relation for the virial coefficients of dilute suspensions of rigid spheres. With a scaling factor for solvent goodness, osmotic pressures of polymer solutions can be predicted with good accuracy. The input parameters needed are the number-average molecular weight of the polymer sample and its intrinsic viscosity in the solvent of interest, as well as its intrinsic viscosity under theta conditions. The intrinsic viscosities can be estimated with sufficient accuracy from tabulated Mark–Houwink coefficients. The model developed contains no adjustable parameters. Comparisons of predicted and reported experimental osmotic pressures are presented, and a method for prediction of second virial coefficients is described.

INTRODUCTION

This article describes a method for predicting the osmotic pressure of polymer solutions from a knowledge of the average molecular weight of the polymer and its intrinsic viscosity in the particular solvent. The model presented here produces estimated osmotic pressure data which agree well with experimental values, and it is a straightforward matter to calculate second virial coefficients from these simulated points by the same methods which are applied to real experimental osmotic pressure values.

The theory used cannot possibly accord with all the properties of real polymers. Its use is justified essentially by its predictive ability and convenience. Essentially, the present method involves a combination of the statistical mechanical derivation of Zimm[1] for the second virial coefficient and the Rudin model[2] for the concentration dependence of the hydrodynamic volume of a solvated polymer.

The relation used here between hydrodynamic volume and virial coefficient is based on a derivation[1] for a dilute suspension of hard spheres. This is equivalent to what is now a standard elementary treatment in the statistical mechanics of gases, where it is sometimes labeled a "restrictive, primitive model"[3] because it handles the interactions of hard spheres, which all have uniform diameter.

An earlier report from this laboratory[4] described predictions of second virial coefficients using an earlier version[5] of the hydrodynamic volume–concentration model. The theory in this article is simpler, less empirical, and more widely applicable.

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THEORY

The hydrodyamic volume of a polymer molecule in solution is denoted $v\epsilon$, where v is the volume of the unsolvated molecule and ϵ is a concentration-dependent, dimensionless swelling factor. At infinite dilution, ϵ equals α_η^3 in Flory's terms.[6] The hydrodynamic volume is assumed to decrease from $v\epsilon$ at infinite dilution to v at a critical concentration, c_x. For any intermediate concentration, the hydrodynamic volume is given by[2]

$$v\epsilon = \frac{4\pi[\eta]M}{9.3 \times 10^{24} + 4\pi N_0 c([\eta] - [\eta]_\theta)}$$ (1)

where $[\eta]$ is intrinsic viscosity (cm^3/g), $[\eta]_\theta$ is intrinsic viscosity of the polymer in the theta condition (cm^3/g), M is molecular weight of the polymer, c is concentration (g/cm^3), and N_0 = Avogadro's number.

The critical concentration, c_x, is defined by

$$c_x = \frac{9.3 \times 10^{24}}{4\pi N_0 [\eta]_\theta} \ (g/cm^3)$$ (2)

and $\epsilon = 1$ for any $c \geq c_x$.

Zimm[1] has derived the following expression for the osmotic second virial coefficient, A_2^*, of a dilute suspension of uniform, rigid spheres with diameter d:

$$A_2^* = \frac{2\pi d^3 N_0}{3M^2}$$ (3)

Since $v\epsilon$ is the equivalent hydrodynamic volume of a polymer molecule in solution, we can write eq. (3) as

$$A_2^* = \frac{4v\epsilon N_0}{M^2}$$ (4)

Substituting eq. (1) for $v\epsilon$ into eq. (3), we obtain

$$A_2^* = \frac{16\pi[\eta]N_0}{M[9.3 \times 10^{24} + 4\pi N_0 c([\eta] - [\eta]_\theta)]}$$ (5)

This expression enables us to calculate a value of A_2^* for each concentration of the polymer solution. Note that the virial coefficients in the statistical mechanical theory are independent of concentration.[1,3] This is not so in the present application because ϵ in eq. (4) is an inverse function of concentration for $0 \leq c \leq c_x$. A_2^* here is of course different from A_2, the conventional second virial coefficient, which is defined to be independent of concentration over the experimental range.

Equation (5) permits the calculation of the osmotic pressure, π, of a polymer solution with concentration c. This follows from

$$\frac{\pi}{c} = \frac{RT}{\overline{M}_n}\left[1 + \frac{A_2^*\overline{M}_n c}{2}\right]^2$$ (6)

The virial expression in eq. (6) follows from the relation between the third and second virial coefficients in the hard sphere model.[7] The second virial coefficient, A_2, can be estimated by the conventional method of plotting calculated $(\pi/c)^{1/2}$ values vs. c.

The approach described is not entirely satisfactory because it does not produce a zero value for A_2 when the polymer is dissolved in a theta solvent. This can be remedied by multiplying A_2^* in eq. (5) by the scaling factor $(1 - [\eta]_\theta)/[\eta]$. The final expression for A_2^* is then

$$A_2^* = \frac{16\pi[\eta]N_0}{M[9.3 \times 10^{24} + 4\pi N_0 c([\eta] - [\eta]_\theta)]}\left[1 - \frac{[\eta]_\theta}{[\eta]}\right] \tag{5'}$$

Equations (5') and (6) give good predictions of osmotic pressures of polymer solutions. It is necessary to know the polymer concentration and an average molecular weight of the sample as well as to be able to calculate $[\eta]_\theta$ and $[\eta]$ in the particular solvent. The theory contains no adjustable parameters.

RESULTS

In order to compare the present theory with exerimental results, it is necessary to examine the conditions under which the various equations are applicable. Firstly, the polymer samples used should be sharp fractions. Secondly, as osmotic pressures are calculated from eq. (6), the results will only be valid at low concentrations or to a good approximation when $(\pi/c) < 3(\pi/c)_0$.[6]

Figures 1 to 7 compare the experimental results obtained from the various sources cited with osmotic pressures calculated using eqs. (5') and (6). Intrinsic viscosities were calculated from the Mark–Houwink equation

$$[\eta] = KM^a \tag{7}$$

and

$$[\eta]_\theta = K_\theta M^{0.5} \tag{8}$$

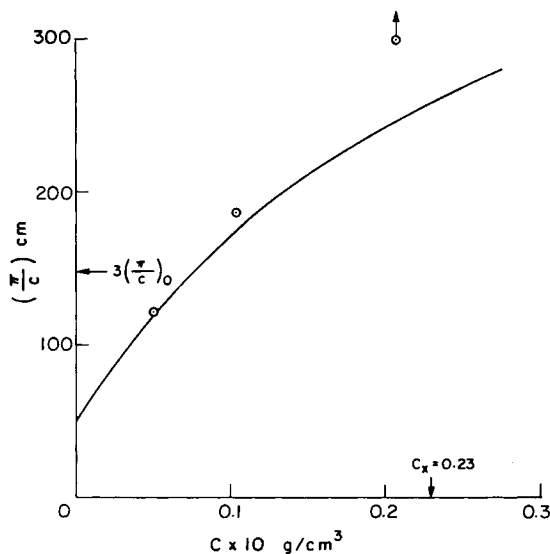The Mark–Houwink constants employed are listed in Table I. Only polymer–

Fig. 1. Osmotic pressure results for 540,000 $\overline{M}_n$ PS in toluene.[8] In Figs. 1 through 7, circles are experimental points and the lines are predicted from eqs. (5') and (6).
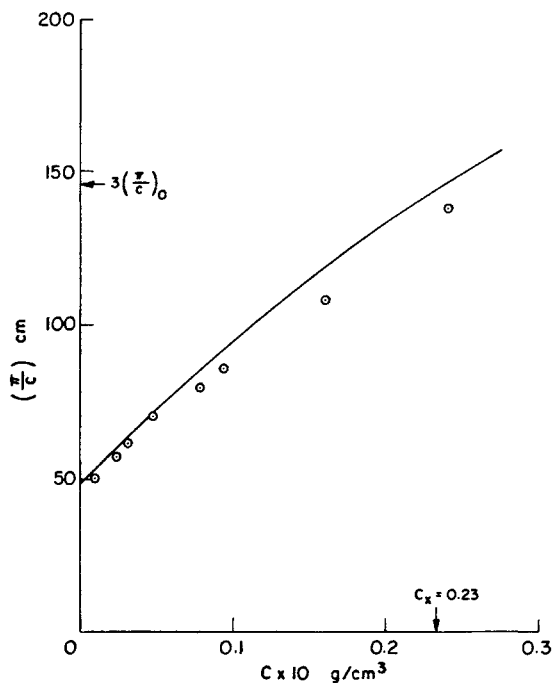
Fig. 2. Osmotic pressure results for 540,000 $\overline{M}_n$ PS in MEK.[9]

solvent systems in which the appropriate Mark–Houwink constants are available have been used in the present study.   Since the requirement of sharp fractions is almost impossible to satisfy in practice, the overall results can be seen to be quite good in most cases for $(\pi/c) < 3(\pi/c)_0$.
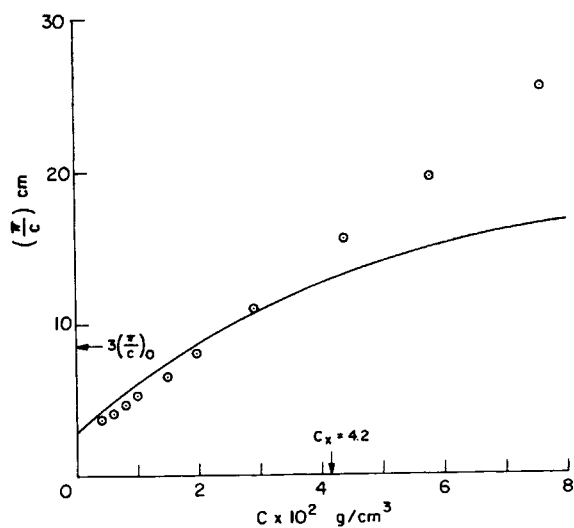

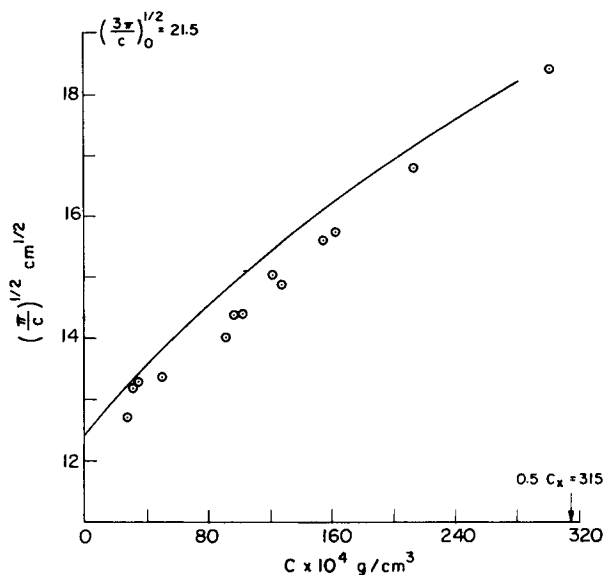Fig. 3. Osmotic pressure results for 90,000 $\overline{M}_n$ PIB in cyclohexane.[9]

Fig. 4. Osmotic pressure results for 166,000 $\overline{M}_n$ PMMA in acetone.[10]

DISCUSSION

The procedures described in this article appear to give good predictions for reduced osmotic pressures of polymer solutions. The input parameters required are the molecular weight of the polymer and its intrinsic viscosity in the solvent of interest as well as its intrinsic viscosity under theta conditions.

Other theories that are capable of calculating osmotic pressures, such as the Flory–Huggins theory[6] and the Fixman method,[19] require thermodynamic parameters which will not be as readily available. The Flory–Huggins theory has been reported to give poor agreement with experimental data, especially at low
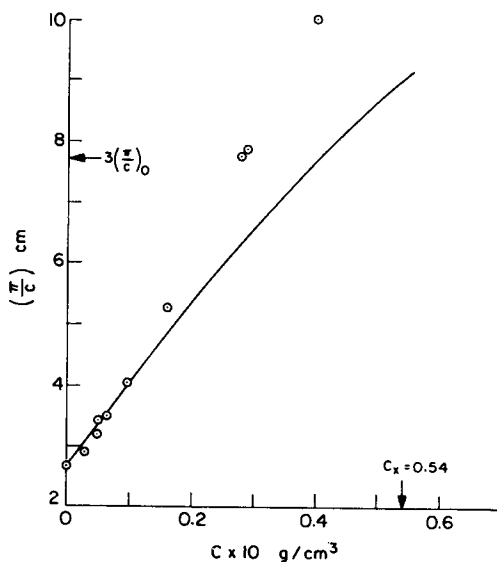

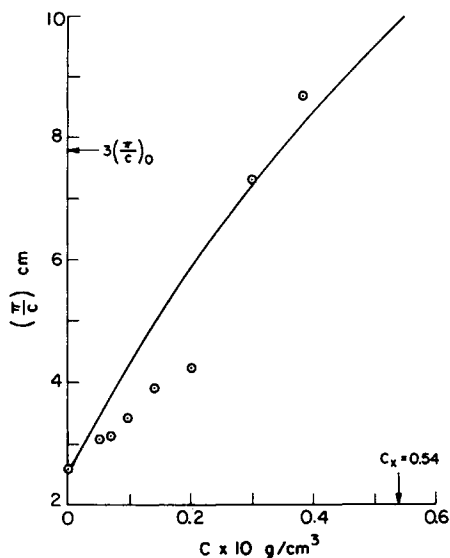Fig. 5. Osmotic pressure results for 98,400 $\overline{M}_n$ PS in chlorobenzene.[11]

Fig. 6. Osmotic pressure results for 97,300 $\overline{M}_n$ PS in dioxane.[11]

concentration.[11,19] The Fixman method appears to be more complex to use than the present procedure, since it requires prior knowledge of the experimental data for estimation of certain parameters in the calculations.

The theory presented here is obviously not completely rigorous. The expression for A_2^* in eq. (3) is based on a derivation[2] which applies only to infinitely dilute suspensions, while the Rudin model gives the change in equivalent hydrodynamic volume of a solvated polymer molecule with finite concentration.
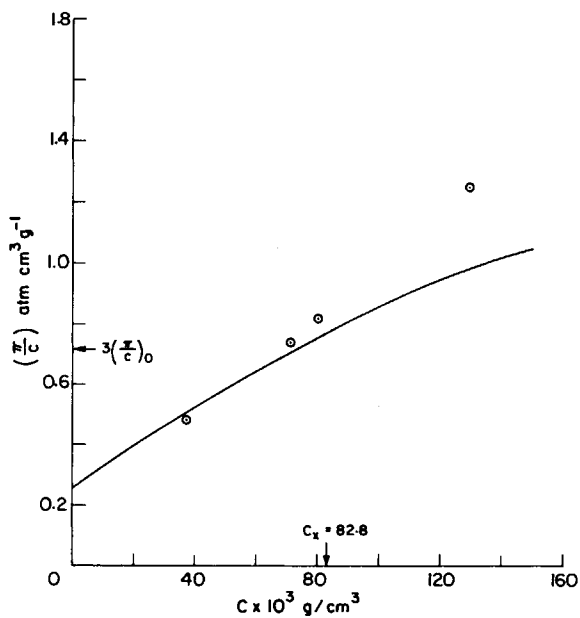

Fig. 7. Osmotic pressure results for 95,600 $\overline{M}_n$ PMMA in acetone.[12]

TABLE I
Mark–Houwink Constants

Polymer	Solvent	Temp., °C	K, $\times 10^3$ cm^3/g	a	Ref.
Poly(methyl methacrylate)[a] (PMMA)	Acetone	30	7.7	0.70	10
Polystyrene[b] (PS)	Toluene	25	17.0	0.69	13
PS	Methyl ethyl ketone	25	19.5	0.635	14
PS	Chlorobenzene	25	7.4	0.749	15
PS	Dioxane	25	15.0	0.694	16
Polyisobutylene[c](PIB)	Cyclohexane	30	26.3	0.69	17

[a] $K_\theta = 48 \times 10^{-3}$ cm^3/g.[10]
[b] $K_\theta = 73 \times 10^{-3}$ cm^3/g.[18]
[c] $K_\theta = 102 \times 10^{-3}$ cm^3/g.[17]

The polymer molecule is regarded as an impermeable sphere, and this is also not true in reality. The scaling factor $1 - ([\eta]_\theta/[\eta])$ likely compensates in some way for the use of Rudin's model for finite concentration behavior with Zimm's relation for infinite dilution. The introduction of such a scaling factor is not without precedent; the temperature dependence of excluded volume parameters is adjusted by similar factors in terms of theta and actual solution temperatures.[20]

The method reported here can also be modified directly to estimate turbidities of polymer solutions from

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w} (1 + A_2^* \overline{M}_w c)^2 \tag{9}$$

where H is an optical constant and τ is the solution turbidity at zero viewing angle. We have not been able to find suitable tabulated light scattering data for such calculations, however. The published results are all reported graphically, to the best of our knowledge, and a comparison between such values and predicted reduced turbidities is not likely to be meaningful.

In Figures 1 to 7, we have also indicated the values of c_x calculated from eq. (2). For the purpose of estimating the conventional second virial coefficient, we have used $0.5c_x$ as the concentration limit. It can be seen that the range of π/c up to this concentration limit is well within the range of $3(\pi/c)_0$, with which there is good agreement with experimental data. We have examined over 140 sets of experimental data and calculated their second virial coefficients. These calculations, together with those obtained using various two-parameter theories, are being reported separately.[21]

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