

Prediction of Second Virial Coefficients from Intrinsic Viscosities

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Synopsis

One of the most readily available characteristics of a polymer sample is its intrinsic viscosity in a particular solvent. This datum can often be estimated reasonably from a single relative viscosity measurement. A number of theories permit the calculation of the second virial coefficient of a polymer/solvent mixture given the intrinsic viscosity and polymer molecular weight. The intrinsic viscosity of the polymer under theta conditions is also needed, but this can be estimated, if necessary, from the molecular weight. This article compares the efficiencies of various alternative models for the prediction of second virial coefficients of a series of polymers and solvents. The most effective technique for this purpose first calculates the concentration-dependent equivalent hydrodynamic volume of a solvated polymer coil. This value is used with a primitive statistical mechanical theory for virial coefficients of hard-sphere suspensions to calculate the osmotic pressure or turbidity of the polymer solution. These simulated experimental values are fitted with a least-squares line as in the real experiment, and the second virial coefficient is derived from the slope. The computations are relatively simple; the average deviation between observed and predicted virial coefficients was less than 16% for a variety of polymer types, molecular weights, and solvents.

INTRODUCTION

A polymer solution theory can be assessed by its ability to predict experimental results. A group of theories has evolved from consideration of the excluded volume effect. These are now often referred to as the two-parameter theory.¹ Two-parameter theories relate dilute polymer solution properties to two basic parameters, i.e., the mean-square end-to-end distance $\langle r \rangle_0$ of a chain in the theta state and the excluded volume parameter z .

The Yamakawa theory² is an example of a two-parameter theory. Recently, Mahabadi and Rudin³ have shown that this model can be used to explain the change in elution volumes with concentrations of polymer solutions in gel permeation chromatography (GPC). In our experience, the Yamakawa theory appears to give the best agreement with experimental results when compared to the other two-parameter theories.

In a different approach, Rudin^{3,4} has proposed a model to account for the concentration dependence of equivalent hydrodynamic volumes of polymer solutions. Although it is simple in derivation, this theory has been shown to be capable of accounting for a modest variety of polymer solution properties. It has given correct estimations of radii of gyration in solution,⁴ corrected for concentration effects in GPC,^{3,4} explained peak shifts in GPC of polymer mixtures,⁵ and predicted osmotic pressures of polymer solutions.⁶

The second virial coefficient is a very important characteristic of polymer

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solutions since its magnitude reflects the solvent strength for the particular polymer. This article considers the prediction of second virial coefficients by several two-parameter theories and the Rudin model. There are many variations of two-parameter theories. We have selected three which are self-consistent combinations for the interpenetration function ψ and the parameter z .

The main objective in this article is to be able to predict second virial coefficients from readily available parameters. The intrinsic viscosity is a suitable parameter for predictive purposes, since it is easily measured and can be approximated quite well from a single relative viscosity measurement.⁷ Few attempts have been made to date to predict second virial coefficients from intrinsic viscosity parameters, so far as we know, although all the models considered here are capable of doing so. The use of any model in this context is justified solely by its ability to predict second virial coefficients from intrinsic viscosity input data. We are not concerned with any other potential shortcomings or virtues of the particular theory.

THEORY

A method for predicting second virial coefficients has been described in a companion article which focussed on the prediction of osmotic pressures of polymer solutions.⁶ Basically, this model simulates the appropriate osmotic pressure experimental data points from

$$\frac{\pi}{c} = \frac{RT}{\bar{M}_n} \left(1 + A_2^* \frac{\bar{M}_n c}{2} \right)^2 \quad (1)$$

in which π is the osmotic pressure of a solution of polymer with number average molecular weight \bar{M}_n and concentration c , and R and T have their usual meanings. The corresponding form for simulation of light scattering results is

$$\frac{Hc}{\tau} = \frac{1}{\bar{M}_w} (1 + A_2^* \bar{M}_w c)^2 \quad (2)$$

where H is an optical constant for the particular solution and apparatus and τ is the turbidity. In eqs. (1) and (2), A_2^* is given by

$$A_2^* = \frac{16\pi N_0 [\eta]}{M(9.3 \times 10^{24} + 4\pi N_0 c([\eta] - [\eta]_\theta))} \left(1 - \frac{[\eta]_\theta}{[\eta]} \right) \quad (3)$$

where $[\eta]$ is the intrinsic viscosity (cm^3/g) of the polymer in the given solvent, $[\eta]_\theta$ is its intrinsic viscosity under theta conditions, c is the concentration (g/cm^3), N_0 is Avogadro's constant, and M is the average polymer molecular weight.

Equation (1) or (2) can be used to predict reduced osmotic pressure (π/c) or turbidity (Hc/τ) data as a function of c . These results are calculated up to a concentration $= 0.5c_x$, where

$$c_x = \frac{9.3 \times 10^{24}}{4\pi N_0 [\eta]_\theta} \quad (4)$$

and c_x is the concentration at which the dimensions of the equivalent hydrodynamic sphere are calculated to have shrunk to their theta condition values.^{3,4} The limit of $0.5c_x$ for these calculations is arbitrary. This corresponds more or less to the highest concentration which might be used in the actual experiments which this model seeks to simulate.

The ostensible virial coefficients A_2^* in eqs. (1) and (2) are concentration dependent because they are related to the radius of the equivalent hydrodynamic sphere which decreases in size with increasing concentration in the concentration region $0 \leq c \leq c_x$. To obtain a concentration-independent second virial coefficient, A_2 , from this model, one plots $(\pi/c)^{1/2}$ [eq. (1)] or $(Hc/\tau)^{1/2}$ [eq. (2)] against c for $0 \leq c \leq 0.5c_x$ and fits a least-squares line to the results to derive A_2 from the slope.

This theory differs from the others considered here in that it involves a direct simulation of raw experimental data points which are then handled exactly as in the real experiment to predict the second virial coefficient of the particular polymer solution.⁶ It will be referred to below as the KR model.

In the two-parameter theory, the second virial coefficient can be written as¹

$$A_2 = 4\pi^{3/2}N_0 \frac{\langle S^2 \rangle^{3/2}}{M^2} \psi \quad (5)$$

in which

$$\psi = \bar{z}h_0(\bar{z}) \quad (6)$$

$$\bar{z} = z/\alpha_s^3 \quad (7)$$

and

$$\alpha_s^2 \equiv \langle S^2 \rangle / \langle S^2 \rangle_0 \quad (8)$$

In the above expressions, $\langle S^2 \rangle$ is the mean square radius of gyration and $\langle S^2 \rangle_0$ is the value of $\langle S^2 \rangle$ under theta conditions.

Various forms of the interpenetration function ψ have been developed. An appropriate expression for z must be selected for each function of ψ such that their derivations are based on the same footing in terms of intramolecular and intermolecular theories of interaction. Three such combinations suggested by Yamakawa¹ are used in the present study. These are:

Combination 1:

Flory-Krigbaum-Orofino theory⁸ of ψ (FKO):

$$\psi = \frac{\ln(1 + 2.30\bar{z})}{2.30} \quad (9)$$

Flory theory of α_s :

$$\alpha_s^5 - \alpha_s^3 = 2.60z \quad (10)$$

Combination 2:

Modified Flory-Krigbaum-Orofino theory¹⁰ of ψ (MFKO):

$$\psi = \frac{\ln(1 + 5.73\bar{z})}{5.73} \quad (11)$$

Modified Flory theory¹¹ of α_s :

$$\alpha_s^5 - \alpha_s^3 = 1.276z \quad (12)$$

Combination 3:

Kurata-Yamakawa theory¹² of ψ (KY):

$$\psi = 0.547[1 - (1 + 3.903\bar{z})^{-0.4683}] \quad (13)$$

Yamakawa-Tanaka theory¹³ of α_s :

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \quad (14)$$

In order to use these theories for the estimation of A_2 from intrinsic viscosity data, it is necessary to make use of equations which do not involve the various radii of gyration. The following relationships of Flory and Fox^{14,15} are useful for this purpose:

$$[\eta] = 6^{3/2}\Phi_0 \frac{\langle S^2 \rangle^{3/2}}{M} \quad (15)$$

and

$$\alpha_s^3 = \alpha_\eta^3 = \frac{[\eta]}{[\eta]_\theta} \quad (16)$$

The proportionality constant Φ_0 is considered below. It appears in all the two-parameter theories and is included in the KR model as well.^{3,4} Elimination of $\langle S^2 \rangle^{3/2}$ in eq. (5) leads to

$$A_2 = \frac{4\pi^{3/2}N_0[\eta]\psi}{6^{3/2}\Phi_0 M} \quad (17)$$

To estimate a value for A_2 , ψ must be calculated according to one of the above theories. Taking combination 3 as an example, one first obtains α_s from eq. (16). Substitution of this value of α_s into eq. (14) gives z , and \bar{z} is then obtained from eq. (7). This is then used in eq. (13) to estimate ψ , and the latter value is finally put into eq. (17) to calculate A_2 .

Various theoretical values of Φ_0 are available. However, a common value which is often obtained is 2.5×10^{23} (with $[\eta]$ and $\langle S \rangle$ in cgs units).¹⁵

It is not our intention here to discuss the validity of the various theories of polymer solution behavior. We are solely concerned with the efficiency of these models in the prediction of second virial coefficients using intrinsic viscosities as the input parameters. So far as we know, this application of these particular theories has not been considered explicitly before.

RESULTS

The theories mentioned above were used to predict second virial coefficients for about 140 polymer samples for which apparently reliable A_2 values were located in the literature. In most cases, the samples selected were fractions with fairly sharp molecular weight distributions. The intrinsic viscosities were calculated from the appropriate Mark-Houwink relations:

$$[\eta] = K\bar{M}_v^a \quad (18)$$

and

$$[\eta]_\theta = K_\theta\bar{M}_v^{0.5} \quad (19)$$

The Mark-Houwink constants used are listed in Table I.

It is not possible to present A_2 values calculated from all three two-parameter theories because of space limitations. Results from the Kurata-Yamakawa (KY) theory have been selected for illustrative purposes, while an overall comparison with the other two models is given below.

Predicted and experimental A_2 values obtained from the KY theory and the

TABLE I
 Mark-Houwink Constants used in Calculation of A_2^a

Polymer	Solvent	Temp., °C	$K_\theta \times 10^3$, mL/g	$K \times 10^3$, mL/g	a	Refer- ence
Poly(methyl methacrylate)	acetone	30	48.0	7.7	0.70	17
Poly(methyl methacrylate)	ethyl acetate	20	48.0 (17)	21.1	0.64	18
Poly(methyl methacrylate)	butanone-2	30	48.0	6.83	0.72	17
Poly(methyl methacrylate)	toluene	30	48.0 (17)	7.0	0.71	19
Polystyrene	toluene	25	72.03	17.0	0.69	20
Polystyrene	butanone-2	25	72.03 (20)	19.5	0.635	21
Poly(methyl methacrylate)	nitroethane	25	48.0 (17)	5.7	0.74	22
Polystyrene	benzene	25	72.03 (20)	9.18	0.743	23
Poly(butyl methacrylate-co-styrene)	butanone-2	35	64.4	5.98	0.75	24
Poly(α -methylstyrene)	toluene	25	71.0	7.06	0.744	25
Poly(vinyl acetate)	butanone-2	25	93.0 (33)	13.4	0.71	26
Poly(methyl methacrylate)	acetone	25	48.0 (17)	7.5	0.70	27
Poly(<i>n</i> -butyl methacrylate)	butanone-2	25	34.0 (34)	9.7	0.68	28
Poly(<i>n</i> -butyl methacrylate)	acetone	25	34.0 (34)	18.4	0.62	28
Polychloroprene	<i>n</i> -butyl acetate	25	113.0	37.8	0.62	29
Polychloroprene	carbon tetrachloride	25	113.0	22.1	0.69	29
Poly(<i>t</i> -butyl acrylate)	butanone-2	25	49.0	3.2	0.80	30
Poly(<i>p</i> -methylstyrene)	toluene	30	70.0	8.86	0.74	31
Poly(<i>p</i> -chlorostyrene)	toluene	30	58.0	11.8	0.65	32
Poly(<i>p</i> -bromostyrene)	toluene	30	45.0	18.2	0.57	32

^a The reference for K_θ is given if this is not taken from the same reference as K and a .

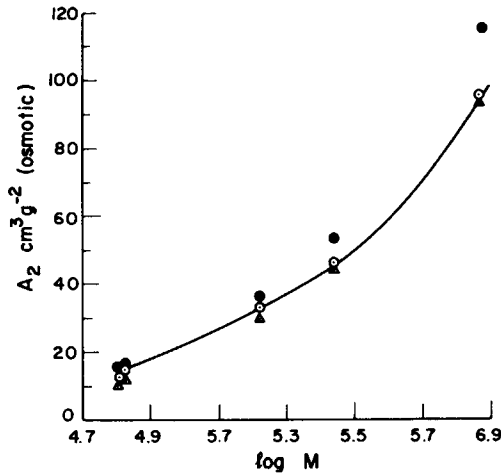


Fig. 1. Osmotic second virial coefficients for poly(methyl methacrylate) in acetone: (O) experimental¹⁷; (●) KR; (▲) KY. The line joins experimental points.

KR model are presented in Figures 1–18. Most of the experimental values are obtained from light scattering measurements. In general, the KR model provides a somewhat better prediction than the KY theory, which estimates virial coefficients which are too small in most cases. This is especially apparent for lower-molecular-weight samples in Figures 2, 3, 6, 8–13, 16, and 17. In Figure 4, however, which deals with very high-molecular-weight polymers, the KY theory

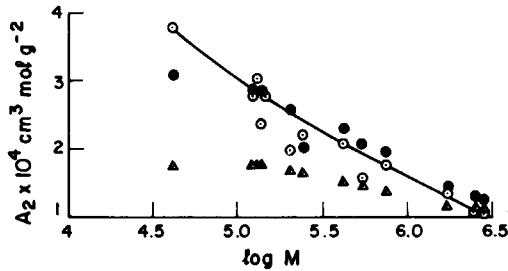


Fig. 2. Light scattering second virial coefficients for poly(methyl methacrylate) in butanone-2.²² Symbols same as in Fig. 1.

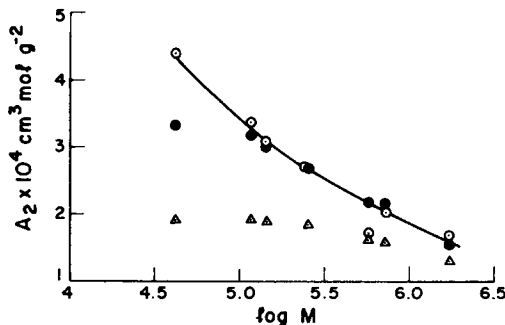


Fig. 3. Light scattering second virial coefficients for poly(methyl methacrylate) in nitroethane.²² Symbols same as in Fig. 1.

predictions are almost exact. Some of the predicted A_2 values from the KR theory are higher than experimental figures, as in Figures 14, 15, and 18.

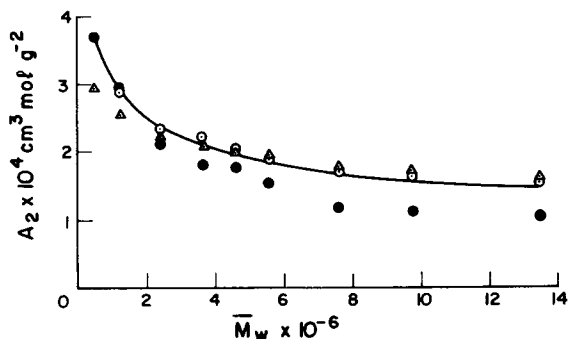


Fig. 4. Light scattering second virial coefficients for high-molecular-weight polystyrenes in benzene.³⁵ Symbols same as in Fig. 1.

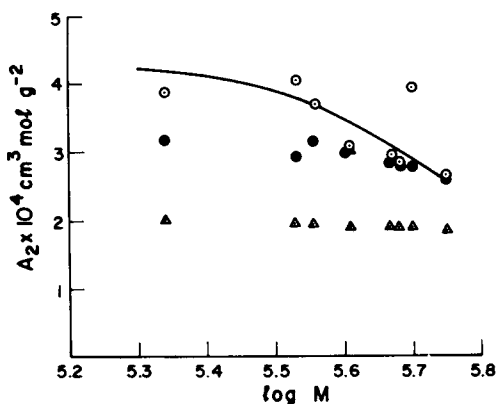


Fig. 5. Light scattering second virial coefficients of poly(butyl methacrylate-co-styrene) in butanone-2.²⁴ Symbols same as in Fig. 1.

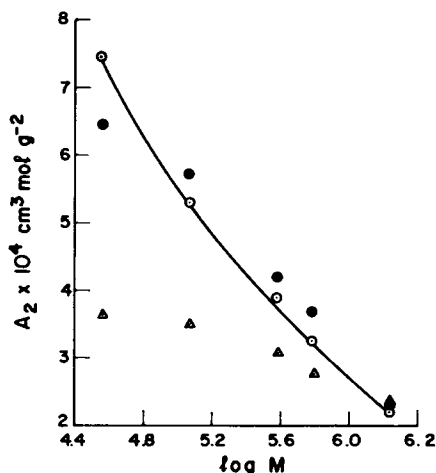


Fig. 6. Second virial coefficients from equilibrium sedimentation measurements³⁶ for polystyrenes in benzene. The predicted values are for light scattering. Symbols same as in Fig. 1.

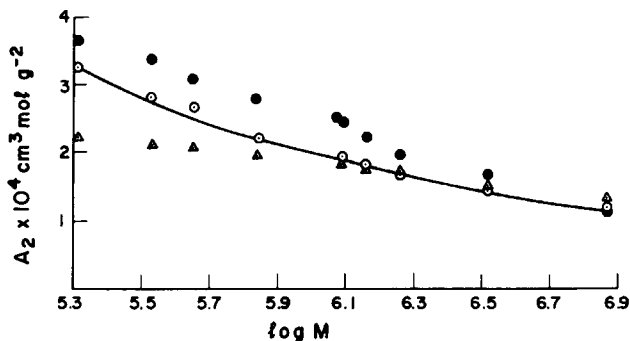


Fig. 7. Light scattering second virial coefficients for high-molecular-weight poly(α -methylstyrenes) in toluene.³⁷ Symbols same as in Fig. 1.

A further comparison of the two theories is provided by the osmotic pressure data of Vink⁴⁰ for a variety of polymers in various solvents. These are generally high-concentration experimental points. The KR theory produces a noticeably better fit to the experimental A_2 values than the KY model, as shown in Table II.

A comparison of the predictions of the four methods is given in Figures 19–22 which show plots of predicted versus experimental A_2 values for all the systems examined. One can judge the merit of each prediction by noting the scatter about the line drawn through the origin with a slope of unity. The two-parameter theories appear to give poor predictions for experimental values of A_2 greater than $3 \times 10^{-4} \text{ cm}^3 \cdot \text{mol}/\text{g}^2$. Generally speaking, this means that the two-parameter theories give good predictions only if the molecular weight is greater than 10^6 .

A quantitative comparison of the above theories can be obtained by calculating the average percentage error over the 140 experimental data examined. Data in which the Mark–Houwink constants are not applicable because the polymer has too low a molecular weight are not taken into consideration. An apparent aberrant data point at $\log M = 5.7$ in Figure 5 is also not used. The average percentage error for each theory is calculated according to

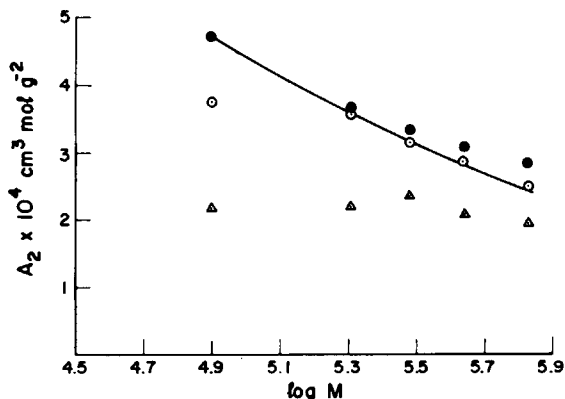


Fig. 8. Light scattering second virial coefficients for lower-molecular-weight samples of poly(α -methylstyrene) in toluene.³⁷ (The experimental A_2 for molecular weight 39,300 has not been used because the original authors reported that its $[\eta]$ was abnormal.) Symbols same as in Fig. 1.

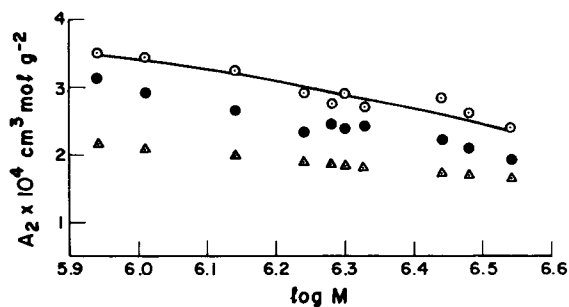


Fig. 9. Light scattering second virial coefficients for poly(vinyl acetate) in butanone-2.²⁶ Symbols same as in Fig. 1.

$$\text{average percentage error} = \frac{\sum_1^N \frac{|\text{experimental} - \text{predicted}|}{\text{experimental}} \times 100}{N} \quad (20)$$

where N is the number (= 140) of experimental data. (Note that only the absolute deviations between predicted and experimental A_2 values are taken into account).

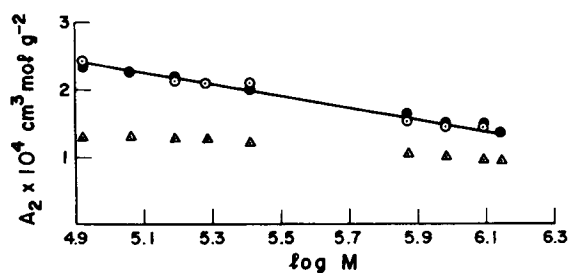


Fig. 10. Light scattering second virial coefficients for poly(methyl methacrylate) in acetone.²⁷ Symbols same as in Fig. 1.

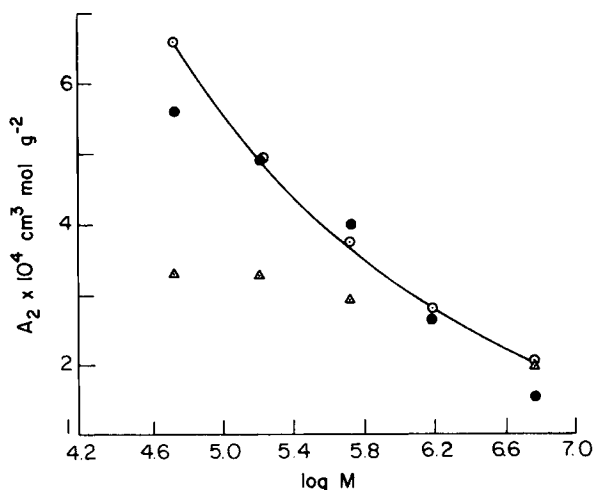


Fig. 11. Light scattering second virial coefficients for polystyrene in tetrahydrofuran.³⁸ Symbols same as in Fig. 1.

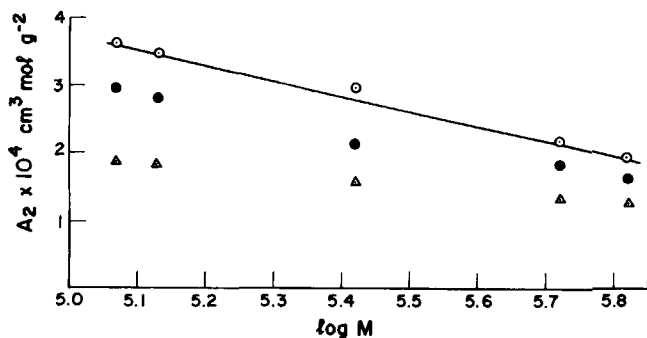


Fig. 12. Light scattering second virial coefficients for poly(*n*-butyl methacrylate) in butanone-2.²⁸ Symbols same as in Fig. 1.

The percent errors obtained for the KR, KY, FKO, and the MFKO theories are 15.6, 25.8, 32.9, and 22.3, respectively.

DISCUSSION

The above results show that the KR model gives generally good predictions of second virial coefficients for a variety of solvents and polymers with different molecular weights. This is convenient, since the estimation of virial coefficients involves simple mathematics in this case.

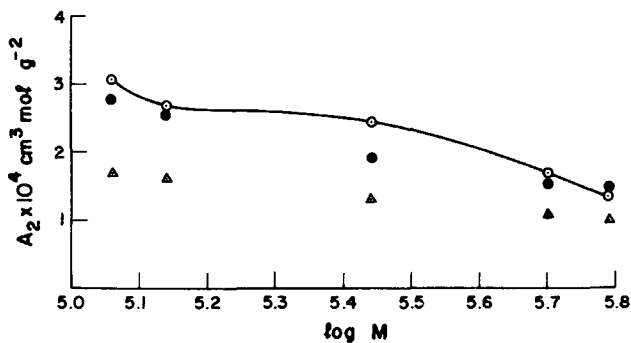


Fig. 13. Light scattering second virial coefficients for poly(*n*-butyl methacrylate) in acetone.²⁸ Symbols same as in Fig. 1.

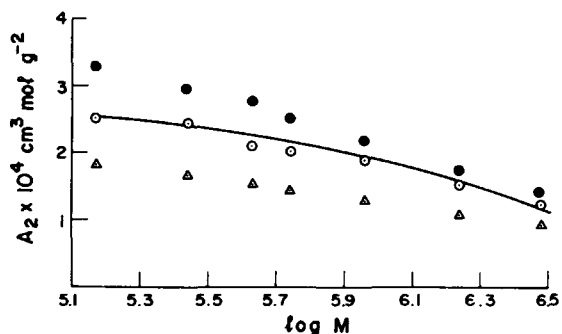


Fig. 14. Light scattering second virial coefficients for polychloroprene in *n*-butyl acetate.³⁹ Symbols same as in Fig. 1.

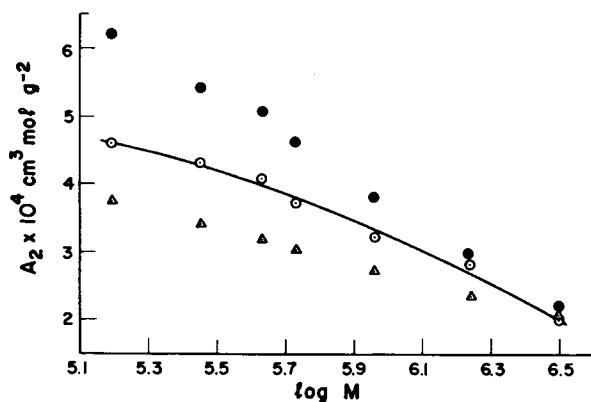


Fig. 15. Light scattering second virial coefficients for polychloroprene in carbon tetrachloride.³⁹ Symbols same as in Fig. 1.

The comparisons in this article are based on the use of intrinsic viscosities as input parameters. We are not concerned with the validity of eqs. (15) and (16), in general. However, since the two-parameter theories rely on these relation-

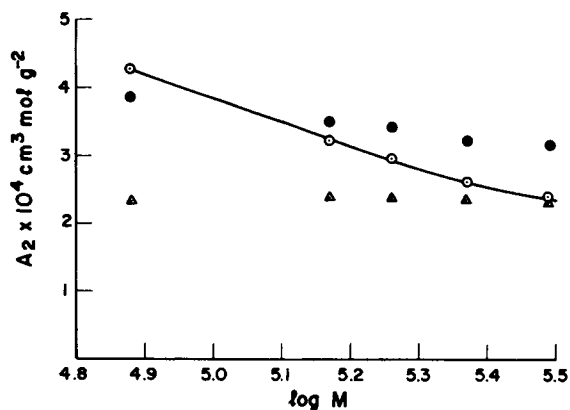


Fig. 16. Light scattering second virial coefficients for poly(*t*-butyl acrylate) in butanone-2.³⁰ Symbols same as in Fig. 1.

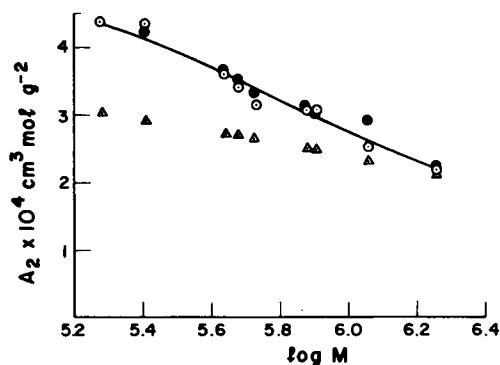


Fig. 17. Light scattering second virial coefficients for poly(*p*-methyl styrene) in toluene.³¹ Symbols same as in Fig. 1.

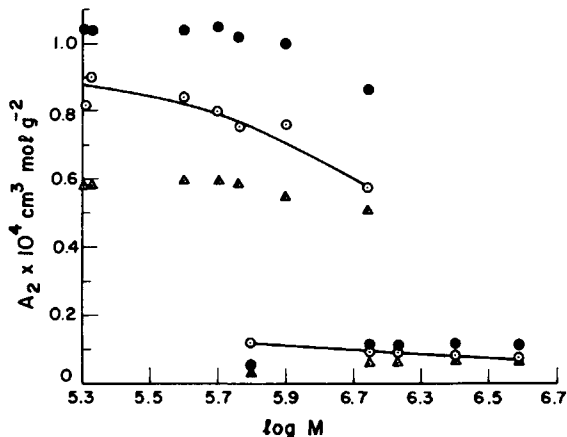


Fig. 18. Light scattering second virial coefficients for poly(*p*-chlorostyrene) in toluene (upper line) and poly(*p*-bromostyrene) in toluene (lower line).³² Symbols same as in Fig. 1.

ships, one should examine the possible improvements in prediction of experimental results when the parameters in these equations are adjusted judiciously. Equation (15) can be changed by using a lower value of the Flory universal constant Φ_0 , as this will increase the value of A_2 estimated by the two-parameter models. An alternative value for this constant is $\Phi_0 = 2.1 \times 10^{23}$ (in cgs units), which is an experimental value often quoted for polydisperse polymers.³³ Also, the equality in eq. (16) can be replaced by⁴¹

$$\alpha_\eta^3 = \alpha_s^{2.43} \quad (21)$$

We have made these substitutions into the calculations, and the average percent errors are shown in Table III. Under the last conditions shown the predictions of the KY theory are improved substantially, while those of the other two-parameter models are not altered for the better. The original Rudin model⁴ used $\Phi_0 = 2.1 \times 10^{21}$ (actually, the Flory constant labelled ϕ' was set at $6^{3/2}\Phi_0$). Substitution of $\Phi_0 = 2.5 \times 10^{21}$ into the formulas for hydrodynamic volume and c_x produces A_2 estimates with an average error of 16.8% for this model.

Krigbaum⁴² suggested the following empirical relation between A_2 and intrinsic viscosities:

$$[\eta] - [\eta]_\theta = 3 \left(\frac{134}{105} \right) \left(\frac{3}{2\pi} \right)^{3/2} \left(\frac{\Phi_0}{N_0} \right) A_2 M \quad (22)$$

TABLE II
Second Virial Coefficient from Vink's Data⁴⁰

Polymer/Solvent	Molecular weight	$A_2 \times 10^4 \text{ cm}^3 \cdot \text{mol/g}^2$ (osmotic)		
		Experimental	KR Theory	KY Theory
PMMA/toluene	89,800	2.65	2.58	1.51
PMMA/acetone	95,600	2.42	2.45	1.39
PMMA/ethyl acetate	103,900	2.82	4.02	2.58
PMMA/butanone-2	100,800	3.24	3.01	1.78
PS/toluene	119,300	5.59	5.65	3.50
PS/butanone-2	550,000	1.41	1.60	0.90

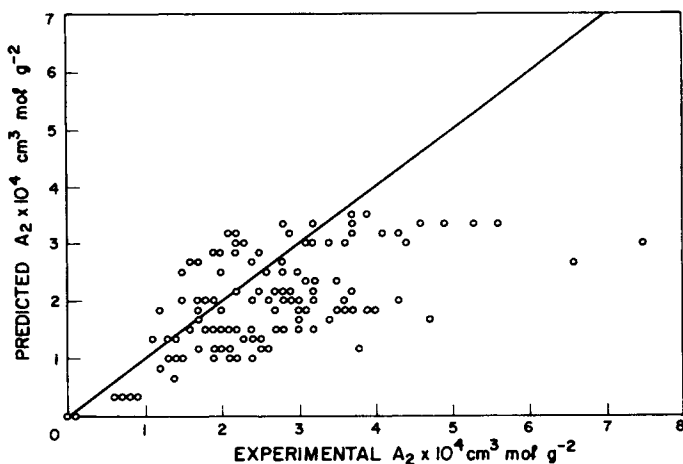


Fig. 19. Comparison of predicted and experimental A_2 values for all the systems studied. The predicted values are from the FKO theory.

TABLE III
Average Percent Errors of Various Theories

$\Phi_0 \times 10^{-23}$, cgs units	Relation between α_s and α_η	Average % error			
		KR	KY	FKO	MFKO
2.5	$\alpha_s = \alpha_\eta$	16.8	25.8	32.9	22.3
2.1	$\alpha_s = \alpha_\eta$	15.6	18.6	30.4	21.6
2.5	$\alpha_\eta^3 = \alpha_s^{2.43}$	16.8	21.5	31.5	21.5
2.1	$\alpha_\eta^3 = \alpha_s^{2.43}$	15.6	17.6	35.3	27.0

With the data used in this study eq. (22) gives an average percent error of 24.9% with $\Phi_0 = 2.1 \times 10^{21}$ and an error of 19.2% with $\Phi_0 = 2.5 \times 10^{21}$ (in cgs units). This relation involves less computation than any of those considered here and produces estimates in reasonable accord with experimental values.

The model described in this and the preceding article on this topic⁶ appears

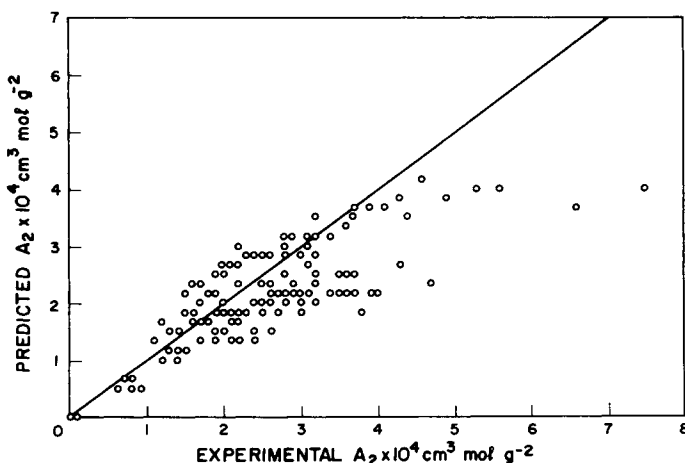


Fig. 20. Comparison of predicted and experimental A_2 values for all the systems reported above. The predicted values are from the MFKO theory.

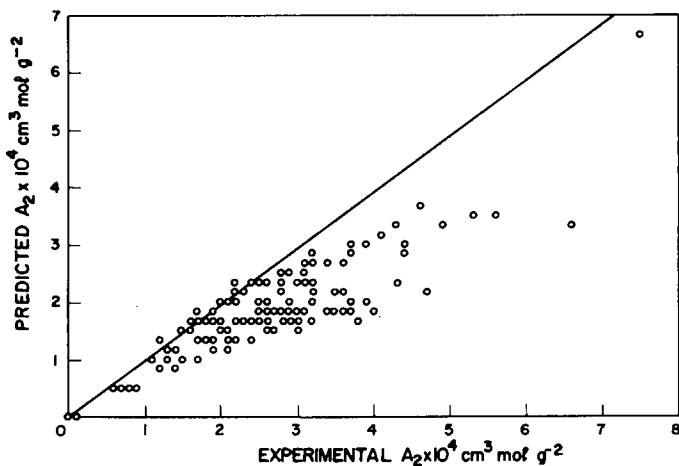


Fig. 21. Comparison of predicted and experimental A_2 values for all the systems reported above. The predicted values are from the KY theory.

to provide the best overall estimates of second virial coefficients for a variety of polymer-solvent combinations (cf. Table II and Fig. 22). It consists essentially of a calculation of a concentration-dependent equivalent hydrodynamic volume for a solvated polymer coil and use of this volume in a primitive statistical mechanical theory for virial coefficients of hard sphere suspensions. It cannot possibly accord with all the characteristics of real polymer solutions, but it can nevertheless serve as a very useful predictive tool despite this limitation.

We have used a model proposed by one of us⁴ to estimate the equivalent dimensions of polymers in solution. Any other theory which predicts these dimensions correctly could be employed equally as well to provide input data for the statistical mechanical dilute suspension model.¹⁶ Thus, it is expected³ that replacement of Rudin's model with Yamakawa's expressions for the concentration dependence of the sizes of equivalent hydrodynamic spheres² would produce equivalent A_2 values with eqs. (1) or (2) and eq. (3).

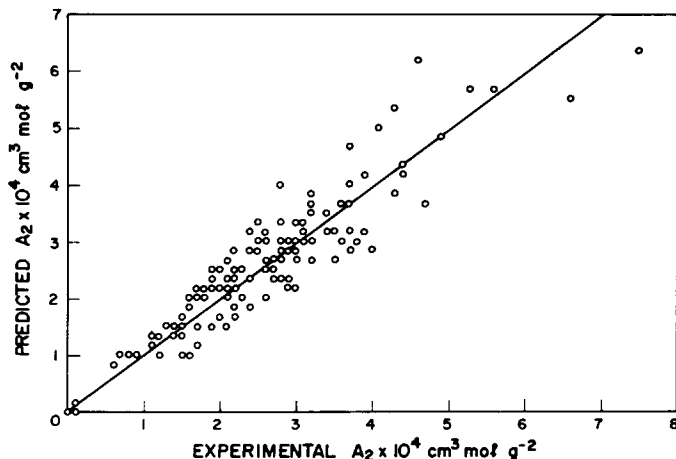


Fig. 22. Comparison of predicted and experimental A_2 values for all the systems reported above. The predicted values are from the KR theory given in this article.

Since the present method simulates the results of the actual experiment from which A_2 is derived, it can also be used to predict colligative properties or turbidity of polymer solutions, as outlined earlier⁶ for osmotic pressure values in particular.

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