Prediction of Flory–Huggins Interaction Parameters from Intrinsic Viscosities

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Synopsis

Previous articles from this laboratory have described a model for predicting the second virial coefficient of a polymer solution given the polymer molecular weight and its intrinsic viscosity in the particular solvent. The same theory is used in this report to calculate values of the Flory–Huggins interaction parameter χ. The method is different in that χ is obtained through manipulation of simulated exprimental data in exactly the same way as in an actual experiment. Agreement between estimated χ values and those obtained at infinite dilutions from membrane osmometry or light scattering is within 2%, on the average. The model accounts for the molecular weight dependence of χ.

INTRODUCTION

The polymer–solvent interaction parameter χ, first introduced by Flory[1] and Huggins,[2] remains an important parameter for characterizing the stability of polymer solutions. For infinitely dilute solutions of very high-molecular-weight polymer, the criterion for polymer solubility is that $\chi \leq 0.5$.[3] Numerous methods have been established which allow one to predict χ or to obtain χ experimentally. These have been reviewed recently by Orwoll.[4]

This article describes a new method for predicting χ using intrinsic viscosities as input parameters. The present approach is unique in the sense that χ is obtained through manipulation of simulated experimental data in exactly the same way as in an actual experiment. The predicted χ values obtained for a number of polymer systems studied are found to be in good agreement with experimental results. Furthermore, the method allows one to calculate the molecular weight dependence of χ.

The present method is based on a model that has recently been used to predict osmotic pressures[5] and osmotic and light-scattering second virial coefficients.[6] The second virial coefficient is of course related to χ by a simple equation. The predicted χ values can be compared directly with experimental χ values obtained by the same experimental methods. At present, the model simulates experimental methods in obtaining the polymer–solvent interaction parameter at infinite dilution of the polymer. Concentration dependence of χ cannot be handled by this method, but this is usually not a serious handicap in determining the suitability of a solvent for a polymer.

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THEORY

As the derivation of the present model has been shown elsewhere,[5,6] only the relevant equations are outlined below.

The osmotic pressure of a polymer solution is given by

$$\frac{\pi}{c} = \frac{RT}{\overline{M}_n}\left\{1 + A_2^*\frac{\overline{M}_n c}{2}\right\}^2 \tag{1}$$

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

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

where H is the optical constant, τ is the turbidity, and $\overline{M}_w$ is the weight-average molecular weight. In eqs. (1) and (2), A_2^* is given by

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

where $[\eta]$ is the intrinsic viscosity (cm³/g) of the polymer in the given solvent, $[\eta]_\theta$ is its intrinsic viscosity under theta conditions, c is the concentration (g/cm³), N_0 is Avogadro's constant, and M is the average polymer molecular weight.

Equations (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 equal to $0.5\, c_X$, where

$$c_X = \frac{9.3 \times 10^{24}}{4\pi N_0[\eta]_\theta} \tag{4}$$

The second virial coefficient A_2 is then obtained in the usual manner by least-squares fitting to the appropriate plots, using either eq. (1) or (2). The χ value is finally obtained through use of

$$A_2 = \frac{\left(\frac{1}{2} - \chi\right)}{\rho_2^2 V_1} \tag{5}$$

where ρ_2 is the density of the polymer (g/cm³) and V_1 is the molar volume of the solvent (cm³/mol).

RESULTS

Orwoll[4] has tabulated an extensive list of χ values. We have calculated χ using the method described above for those systems in which the experimental χ values were obtained from osmotic pressure measurements. The input parameters of η and η_θ were obtained from the Mark-Houwink equations

$$[\eta] = KM^a \tag{6}$$

and

$$[\eta]_\theta = K_\theta M^{0.5} \tag{7}$$

The K, K_θ, a, and density values of polymers used are tabulated in Tables I and

TABLE I
Mark–Houwink Constants

Polymer	Solvent	Temp., °C	$K \times 10^3$, mL/g	a	Reference
Poly(methyl methacrylate) (PMMA)	acetone	25	7.5	0.7	7
PMMA	benzene	20	8.35	0.73	8
PMMA	chloroform	25	4.8	0.8	9
PMMA	toluene	25	7.1	0.73	10
PMMA	tetrahydrofuran	25	12.8	0.69	11
PMMA	4-heptanone	33.8	48.0	0.50	12
PMMA	n-butylchloride	35.4	50.5	0.50	13
Polystyrene (PS)	chlorobenzene	25.7	7.4	0.749	19
PS	cyclohexane	34	82.0	0.50	15
PS	cyclohexane	45	34.7	0.575	19
PS	methyl ethyl ketone	25	39.0	0.58	16
PS	benzene	25	9.18	0.743	17
PS	ethylbenzene	25	17.6	0.68	18
PS	toluene	25	17.0	0.69	16
PS	dichloroethane	25	21.0	0.66	16
Poly(vinyl chloride) (PVC)	cyclohexanone	30	16.3	0.77	19
PVC	chlorobenzene	30	71.2	0.59	19
Poly(vinyl acetate) (PVA)	acetone	25	21.4	0.68	21
PVA	benzene	30	22.0	0.65	14
PVA	dioxane	25	11.4	0.74	21
PVA	methyl ethyl ketone	25	13.4	0.71	22
Natural rubber (NR)	benzene	30	18.5	0.74	23
NR	toluene	25	50.2	0.667	24
Poly(p-chloro-styrene)	toluene	30	13.0	0.64	25
Poly(p-chloro-styrene)	chlorobenzene	30	2.19	0.80	26
Polypropylene (PP)	benzene	25	27.0	0.71	27
PP	cyclohexane	25	16.0	0.80	27
Cellulose triacetate	ethanol/methylene chloride (20/80 vol)	25	13.9	0.834	28
Poly(dimethyl-siloxane)	methyl ethyl ketone	20	81.0	0.50	29
Poly(dimethyl-siloxane)	benzene	20	12.0	0.68	30
Poly(dimethyl-siloxane)	toluene	20	20.0	0.66	31

TABLE II
K_θ and Densities[a] of Polymers

Polymer	Density, g/cm³	Temp., °C	$K_\theta \times 10^3$ mL/g	Reference
Poly(methyl methacrylate)	1.188	30	48.0	12
Polystyrene	1.04	25	72.03	20
Poly(vinyl chloride)	1.41	25	100.0	19
Poly(vinyl acetate)	1.19	25	93.0	19
Natural rubber	0.906	20	130.0	19
Poly(dimethylsiloxane)	0.98	25	80.0	19
Poly(p-chlorostyrene)	1.04	30	50.0	19
Polypropylene	0.85	30	156.0	19
Cellulose triacetate	1.296	25	108.0	19

[a] Densities of polymers are the amorphous densities obtained from Ref. 19.

II. Molecular weights were obtained from the cited references. Only those systems in which the Mark–Houwink constants are applicable have been considered. Physical constants of solvents used can be found in Table III.

The results obtained are shown in Table IV. The agreement between experimental and predicted results is very good. The mean estimation error for the 66 χ values considered is only 1.9%.

The present model predicts an increase in χ with molecular weight. Three cases, in which the experimental results are available for comparison, are shown in Figures 1–3. The agreement is generally good, considering the fact that χ values are plotted on a very sensitive scale.

DISCUSSION

The results presented have shown that the present model can be used to predict χ values that are in good accordance with experimental results. Any other theory which is capable of giving the second virial coefficient, A_2, can also be used

TABLE III
Parameters of Solvents Used in Calculations[33]

Solvent	Density, g/cm³	Molar volume, cm³/mol
Acetone	0.7899	73.53
Benzene	0.8787	88.91
n-Butyl chloride	0.8862	104.46
Chloroform	1.4832	80.49
1,1-Dichloroethane	1.1757	84.2
Cyclohexane	0.7786	108.10
Dioxane	1.0337	85.25
Methyl ethyl ketone	0.8054	89.5
Ethylbenzene	0.8670	122.7
4-Heptanone	0.8174	139.7
Toluene	0.8669	106.2
Tetrahydrofuran	0.9514	71.6
Cyclohexanone	0.9478	104.2
Chlorobenzene	1.1058	102.1
Methylene chloride	1.3266	64.0

TABLE IV
Comparison of Experimental and Predicted χ Values

Polymer/solvent System	Molecular weight $\times 10^{-5}$	Temp., °C	Experimental χ	Predicted χ	% Error	Reference
Poly(p-chlorostyrene)						
Chlorobenzene	3.16	30	0.465	0.478	2.80	34
Toluene	4.63	30	0.489	0.486	0.61	34
Poly(dimethylsiloxane)						
Methyl ethyl ketone	2.9	25	0.5	0.5	0	35
Toluene	1.04	20	0.445	0.461	3.6	36
Natural rubber						
Benzene	0.4	25	0.40	0.40	0	37
Poly(methyl methacrylate)						
Acetone	1.29	27	0.480	0.477	0.63	38
Benzene	1.325	27	0.440	0.449	2.05	38
n-Butylchloride	46.0	32	0.502	0.50	0.4	39
Chloroform	1.215	27	0.440	0.440	0	38
4-Heptanone	2.1	38	0.501	0.500	0.2	39
Tetrahydrofuran	1.31	27	0.460	0.460	0	38
Toluene	1.29	27	0.450	0.448	0.44	38
Polypropylene						
Benzene	3.08	25	0.498	0.445	10.6	27
Cyclohexane	1.38	25	0.420	0.359	14.5	27
Polystyrene						
Toluene	8.4	27	0.437	0.467	6.87	40
Toluene	4.73	27.5	0.444	0.460	3.60	41
Toluene	2.44	28	0.430	0.449	4.42	42
Toluene	3.73	30	0.456	0.454	0.44	34
Toluene	6.12	30	0.463	0.460	0.65	43
Chlorobenzene	3.88	30	0.454	0.460	1.32	34
Cyclohexane	4.4	44	0.494	0.490	0.81	47
Cyclohexane	4.4	34	0.5	0.5	0	47
Benzene	4.39	25	0.455	0.463	1.76	49
Ethylbenzene	4.4	25	0.450	0.456	1.33	49
Cyclohexane	8.4	49	0.495	0.489	1.21	40
Methyl ethyl ketone	18.1	27	0.490	0.491	0.20	48
Methyl ethyl ketone	8.4	27	0.486	0.488	0.41	40
Methyl ethyl ketone	4.73	27.5	0.488	0.485	0.62	41
Methyl ethyl ketone	2.44	28.0	0.471	0.482	2.34	42
Methyl ethyl ketone	*8.4	49	0.485	0.488	0.62	40
Methyl ethyl ketone	*2.44	52	0.474	0.482	1.69	42
Methyl ethyl ketone	0.146	25	0.476	0.471	1.05	16
Methyl ethyl ketone	0.161	25	0.478	0.471	1.46	16
Methyl ethyl ketone	0.237	25	0.477	0.471	1.26	16
Methyl ethyl ketone	0.62	25	0.481	0.475	1.25	16
Methyl ethyl ketone	1.14	25	0.484	0.478	1.24	16
Methyl ethyl ketone	1.17	25	0.481	0.478	0.62	16
Methyl ethyl ketone	1.23	25	0.483	0.478	1.03	16
Methyl ethyl ketone	2.30	25	0.489	0.482	1.43	16
Methyl ethyl ketone	3.18	25	0.488	0.483	1.03	16
Methyl ethyl ketone	5.07	25	0.491	0.485	1.22	16
Methyl ethyl ketone	9.40	25	0.491	0.488	0.61	16
Methyl ethyl ketone	9.80	25	0.490	0.488	0.41	16
Methyl ethyl ketone	13.2	25	0.492	0.489	0.61	16
Methyl ethyl ketone	16.1	25	0.492	0.490	0.41	16
Methyl ethyl ketone	17.55	25	0.491	0.491	0	16

TABLE IV   *(Continued from previous page.)*

Polymer/solvent System	Molecular weight $\times 10^{-5}$	Temp., °C	Experimental χ	Predicted χ	% Error	Reference
Methyl ethyl ketone	1.23	25	0.480	0.478	0.42	50
Methyl ethyl ketone	2.66	25	0.483	0.483	0	50
Methyl ethyl ketone	4.70	25	0.484	0.485	0.21	50
Methyl ethyl ketone	5.54	25	0.494	0.486	1.62	50
Methyl ethyl ketone	6.60	25	0.489	0.487	0.41	50
Methyl ethyl ketone	8.80	25	0.489	0.488	0.20	50
Methyl ethyl ketone	11.9	25	0.489	0.489	0	50
Methyl ethyl ketone	15.0	25	0.491	0.490	0.20	50
Dichloroethane	0.161	25	0.434	0.446	2.77	16
Dichloroethane	0.237	25	0.434	0.446	2.77	16
Dichloroethane	1.38	25	0.454	0.460	1.32	16
Dichloroethane	5.07	25	0.468	0.471	0.64	16
Dichloroethane	5.62	25	0.468	0.473	1.07	16
Dichloroethane	16.1	25	0.475	0.482	1.47	16
Dichloroethane	17.8	25	0.478	0.483	1.05	16
Poly(vinyl chloride) Cyclohexanone	0.99	29.8	0.240	0.210	12.50	44
Poly(vinyl acetate)						
Acetone	1.4	25	0.437	0.442	1.14	45
Benzene	2.12	20	0.420	0.466	10.95	46
Dioxane	1.3	25	0.407	0.423	3.93	45
Methyl ethyl ketone	8.4	25	0.440	0.459	4.32	45
				Average % error	1.89	

* K and a used were for 25°C.

to estimate χ with eq. (5). We have, however, already compared various methods for estimating A_2 and shown that the present model gives the most generally reliable predictions.[6] It will therefore also provide the best route to χ through A_2.
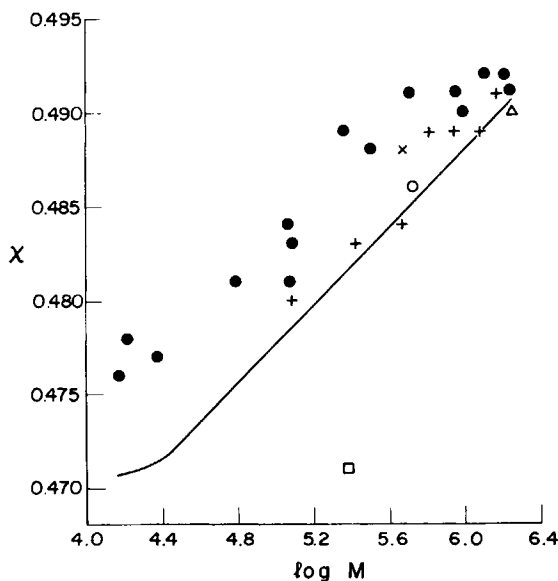

Fig. 1. Molecular weight dependence of χ for polystyrene/methyl ethyl ketone at 25°C. The solid line is predicted: (●) Ref. 16; (+) Ref. 50; (△) Ref. 48; (○) Ref. 40; (×) Ref. 41; (□) Ref. 42.
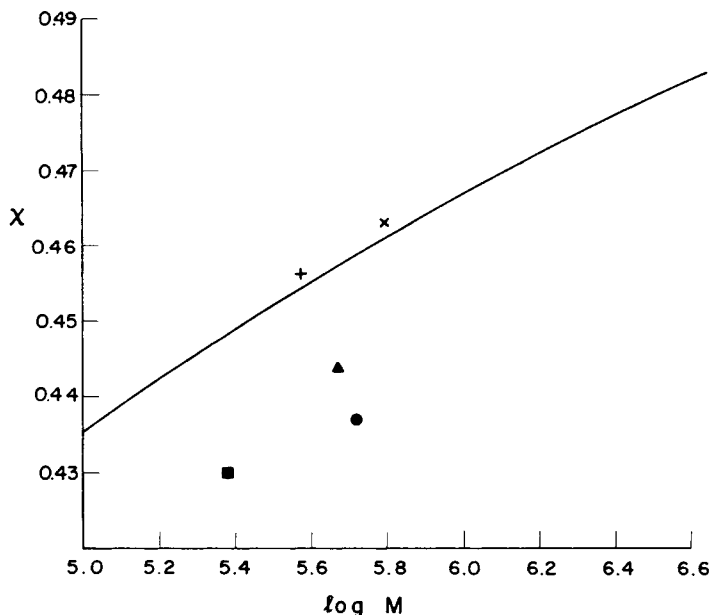
Fig. 2. Molecular weight dependence of χ for polystyrene/toluene at 25°C. The solid line is predicted. (●) Ref. 40; (▲) Ref. 41; (+) Ref. 34; (✕) Ref. 43; (■) Ref. 42.

Other predictive methods which do not consider second virial coefficients are also available to calculate χ. These, however, normally disregard the effect of molecular weight. They have not been subjected to as rigorous a test as the model presented here. Sheehan and Bisio,[51] for example, have compared the methods of Hildebrand,[52] Blanks–Prausnitz,[53] and Shvarts[54] for 16 polymer–solvent systems (12 polymer–solvent systems for the Shvarts method). The estimation errors were reported as 19.7, 16.6, and 8.8%, respectively. Table V
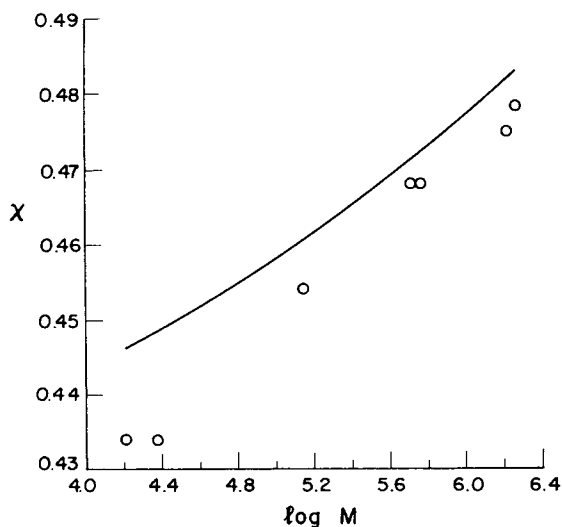

Fig. 3. Molecular weight dependence of χ for polystyrene/dichloromethane at 25°C. The solid line is predicted and the data points are from Ref. 16.

TABLE V
Calculated and Experimental χ for Poly(Vinyl Acetate),[45] a Comparison of Different Theoretical Methods

Solvent	Experimental Temp., °C	Experimental χ	Hildebrand χ	Hildebrand Error, %	Blanks–Prausnitz χ	Blanks–Prausnitz Error, %	Shvarts method χ	Shvarts method Error, %	This model χ	This model Error, %
Acetone	25	0.437	0.354	19	0.416	4.8	0.43	1.6	0.442	1.1
Methyl ethyl ketone	25	0.429	0.344	19.8	0.354	17.5	0.364	15.2	0.442	3.0
Dioxane	25	0.407	0.356	12.5	0.514	26.3	0.433	6.4	0.423	3.9
Average error				17.1		16.2		7.7		2.7

shows three of the experimental systems considered in which χ was obtained by osmotic pressure measurements. The results calculated using the present model are shown in the last two columns for comparison and are clearly in best accord with the experimental values.

The use of intrinsic viscosities as input parameters for calculating χ has been considered before by Bristow and Watson.[55] According to their method, χ is obtained from the expression

$$0.5 + x^{-1/2} - \chi = \frac{V_1}{2C_M K_\theta M} \left\{ \frac{[\eta]^{5/3}}{[\eta]_\theta^{2/3}} - [\eta] \right\} \tag{8}$$

in which x is the chain length, V_1 is the molar volume of the solvent, and M is the molecular weight. $C_M K_\theta$ is given by the equation[32]

$$C_M K_\theta = 1.4 \times 10^{-24} (\bar{v}_2 / V_1) \Phi \tag{9}$$

where $\bar{v}_2$ is the specific volume of the polymer and Φ is Flory's constant (2.5×10^{23} cgs units). These authors, however, did not compare their χ values with those of other experimental methods. Mangaraj[56] has pointed out that their χ values were not in good agreement with values obtained by other methods. We have used the method described by Bristow and Watson to calculate χ for the 66 systems mentioned above. An average estimation error of 8.2% was obtained. This is very much higher than the value of 1.9% using the present model.

We have also carried out some calculations for χ in which the experimental method used did not involve the second virial coefficient. The results with the systems that we have examined are shown in Table VI. One should not attempt to compare the absolute values of χ in these cases, but rather their magnitudes. There are two factors to be considered. Firstly, for the swelling method, the molecular weights quoted were only very approximate values as changes of molecular weights occurred during compounding of the rubbers with crosslinking agents. Secondly, the values of χ quoted were not at infinite polymer dilutions, except for the combination of cellulose acetate/methylene chloride. In the latter system, one sees that there is very good agreement between the experimental and theoretical results. Care must be exercised in comparing the two, insomuch as χ is a function of concentration and molecular weight. Even if the latter two conditions are similar, differences may arise due to certain unreliabilities in the methods themselves. A case in point is the swelling method in which an assumed χ has to be used in the first place for calibration purposes.

TABLE VI
Experimental and Calculated χ (Different Experimental Methods)

Polymer/solvent system	Temp. (°C)	Mol. Wt.	Method	χ Value		Reference
				Experimental	Predicted	
Poly(vinyl chloride)						
Chlorobenzene	53	500,000[a]	swelling	0.53	0.41	57
Poly(dimethylsiloxane)						
Benzene	25	780,000	swelling	0.52	0.49	58
Toluene	25	780,000	swelling	0.47	0.48	58
Natural rubber						
Benzene	25	220,000[b]	GLC[c]	0.46	0.43	59
Toluene	25	220,000[b]	GLC	0.36	0.41	59
Cellulose acetate						
Methylene chloride	25	157,000	vapor pressure	0.3	0.296	60

[a] Assumed molecular weight (paper quoted "high molecular weight").
[b] Private communication from B. M. E. van der Hoff (University of Waterloo).
[c] Gas–liquid chromatography.

The present model aims to simulate the osmotic (or light scattering) method of obtaining χ, and we have shown that it can be used for a variety of polymer solvent systems. The effect of molecular weight is also accounted for. Although the method reported here cannot be employed for high polymer concentrations, it is hoped that it will still serve as a useful engineering tool.

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