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Evaluation of Excluded Volume Parameter for Polymer-Solvent Systems

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ABSTRACT

The short-range interaction parameter, K_{θ} , and the excluded volume parameter, B , for several polymer-solvent systems were evaluated from the experimental data of intrinsic viscosity, second virial coefficient as obtained from sedimentation equilibrium experiments, and also through a procedure in which both kinds of experimental data are simultaneously employed. The values of the parameters so obtained are in reasonable agreement except for the case of the Stockmayer-Fixman relation.

INTRODUCTION

Since the theory of excluded volume effect in a polymer chain was first developed by Flory [1], a number of attempts have been made to

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solve this problem, and it has been one of the central problems in the polymer solution literature. In a series of papers Yamakawa and co-workers [2-6] suggested several theoretical and empirical relations for the dependence of the excluded volume parameter, B , with the more fundamental observable properties such as intrinsic viscosity $[\eta]$, expansion factor α , second virial coefficient A_2 , and other polymer chain dimensions. However, in most theories of polymer solutions, the two types of expansion factors have been routinely defined as

$$\alpha_{\eta}^3 = [\eta]/[\eta]_{\theta} = [\eta]/K_{\theta}M^{1/2} \quad (1)$$

and

$$\alpha_s^2 = \langle R_G^2 \rangle / \langle R_G^2 \rangle_0 \quad (2)$$

where $[\eta]$ and $[\eta]_{\theta}$ represent the intrinsic viscosities in a good solvent and in "theta" solutions, respectively; similarly, $\langle R_G^2 \rangle$ and $\langle R_G^2 \rangle_0$ are the mean square radii of gyration as obtained from light-scattering experiments on polymer solutions in good and ideal solvents, respectively; M is molecular weight of the polymer and K_{θ} is a constant.

A widely used relationship between the excluded volume parameter, intrinsic viscosity, and molecular weight was given by Stockmayer and Fixman [7]:

$$[\eta] = K_{\theta}M^{1/2} + 0.51\Phi BM \quad (3)$$

Here, Φ is considered to be a universal constant for all flexible linear macromolecules, although there is some evidence that it may decrease with an increase in molecular weight and the solvent power. When one employs Relation (3) graphically to plot the quantity $[\eta]M^{-1/2}$ versus $M^{1/2}$, the intercept would yield K_{θ} and the limiting slope would yield the excluded volume parameter B_{θ} . This procedure works reasonably well for rather poor solvents; the dependences for good solvents are curved and the extrapolation is ambiguous. Several other analytical forms of the function α_{η}^3 have been offered [8-10] to improve the linearity of the plot and the usefulness of the extrapolation procedure. None of these trials was very successful [11]. Also, the values of B as calculated from Eq. (3) were widely different from those calculated by different procedures. Alternatively, Tanaka and co-workers [6] suggested this difference to be due to a wrong choice in the numerical coefficient and proposed the following empirical relation:

$$[\eta] = 1.05K_{\theta} M^{1/2} + 0.287\Phi B M \quad (4)$$

However, the restriction imposed on the use of the equation is that α_{η}^3 should be in the range $1 \leq \alpha_{\eta}^3 \leq 2.5$. Quite recently, Chiantore and Guita [12] were able to relax this condition and, ignoring the difference between the two types of expansion factors (i.e., α_s and α_{η}) [13, 14], they proposed the relation

$$[\eta] = K_{\theta} M^{1/2} \left\{ 0.541 + 0.459 \left[1 + 6.04(3/2\pi)^{3/2} \frac{\Phi B}{K_{\theta}} M^{1/2} \right] \right\}^{3/2} \quad (5)$$

Thus, using Eq. (5), one can compute the parameters K_{θ} and B from intrinsic viscosity data without any restrictions on the values of α_{η} . It should be noted that Eqs. (3)-(5) are valid for only monodisperse polymers, and a suitable correction factor has to be used to account for polydispersity if weight-average molecular weight \bar{M}_w has to be used in place of M in these relations. The correction factor q_{MH} has been calculated [12] assuming a Lansing-Kraemer distribution of the molecular masses in the polymer samples studied. The quantity q_{MH} is given by

$$q_{MH} = \exp \{ \ln(u)/2x \} \quad (6)$$

where $u = \bar{M}_z/\bar{M}_w$ and $x = 1/a(a - 1)$, a being the Mark-Houwink exponent. Therefore Eqs. (3)-(5) can be used to fit $[\eta]/(q_{MH}\bar{M}_w^{1/2})$ values plotted versus $\bar{M}_w^{1/2}$ from the experimental data of Table 1.

A second approach to the same problem has been suggested through the use of second virial coefficients. Thus

$$A_2 = \frac{N_A}{2} B h(\bar{z}) \quad (7)$$

where N_A is Avogadro's number and $h(\bar{z})$, according to Kurata et al. [5], has been given as

$$h(\bar{z}) = \frac{1 - (1 + 3.903\bar{z})^{-0.4683}}{1.828\bar{z}} \quad (8)$$

with

$$\bar{z} = z/\alpha_s^3 \quad (9)$$

TABLE 1. Molecular Weight, Intrinsic Viscosity, Second Virial Coefficient, Polydispersity, and Polymolecularity Correction Factors for Polymer-Solvent Systems at 20°C

Sample abbreviation	$M_w \times 10^{-3}$	$[\eta]$ (cm ³ /g)	$A_2 \times 10^4$ (cm ³ mol/g ²)	u	q_{MH}	q_w	Ref.
<u>1. Polystyrene in Benzene at 20°C</u>							
PS1	35.6	23.25	7.24	1.010	0.999	1.001	15
PS2	117	52.4	5.19	1.015	0.998	1.002	
PS3	186	73.2	4.67	1.015	0.998	1.002	
PS4	372	126.7	3.65	1.07	0.993	1.009	
PS5	596	179.4	3.32	1.17	0.983	1.021	
PS6	1750	-	2.22	1.55	0.953	1.065	
<u>2. Polystyrene in Bromobenzene at 20°C</u>							
PS1	35.5	23.22	6.38	1.010	0.999	1.001	15
PS2	114	52.3	5.08	1.015	0.998	1.002	
PS3	181	72.0	4.43	1.015	0.998	1.002	
PS4	366	123.9	3.17	1.07	0.993	1.009	
PS5	596	179.4	2.97	1.17	0.983	1.022	
PS6	1750	460.3	2.15	1.55	0.953	1.068	
<u>3. Polyacrylamide in 0.2 M Sodium Chloride at 20°C</u>							
PAA1	255	133	3.06	1.44	0.961	1.120	16
PAA2	616	268	3.31	1.62	0.949	1.167	
PAA3	1010	379	3.12	1.67	0.946	1.180	
PAA4	2430	640	2.90	1.73	0.942	1.195	
PAA5	2750	752	2.81	1.52	0.956	1.141	

Within the framework of two parameter theory [2], the parameters z and α were defined as

$$z = (3/2\pi)^{3/2} \frac{\Phi B}{K_\theta} M^{1/2} \quad (10)$$

and

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \quad (11) \quad (\text{See note on page 1291.})$$

Thus, by plotting A_2^*/q_{sw} as a function of $\bar{M}_w^{1/2}$ according to Eq. (7), one obtains the values of K_θ and B by a nonlinear least squares method.

From a combined use of experimental data on intrinsic viscosity and second virial coefficient, Chiantore and Guida [12] have proposed the relation

$$\frac{A_2 M}{[\eta]} = 0.829 \frac{N_A}{\Phi} \left[1 - (1 + 1.288 \Phi B \frac{M}{[\eta]})^{-0.4683} \right] \quad (12)$$

A correction to the polydispersity has been made using the relation

$$q_w = \frac{\exp[\sigma^2(2-\nu)^2/2] + 3 \exp[5\sigma^2(2-\nu)^2/18]}{4 \exp[\sigma^2(2-\nu)/2]} \quad (13)$$

Here ν has been evaluated (along with A_0) through an iterative procedure (initially taking $q_w = 1$) using the relation

$$\ln(A_2^*/q_w) = -\nu \ln \bar{M}_w + \ln A_0 \quad (14)$$

The data for q_w are presented in the last column of Table 1. From a plot of $(A_2^* \bar{M}_w q_{MH}/[\eta] q_w)$ versus $\bar{M}_w q_{MH}/[\eta]$ for polydisperse samples, the excluded volume parameter B can be evaluated by a nonlinear least squares methods from viscosity and light-scattering or sedimentation equilibrium data.

RESULTS AND DISCUSSION

Table 1 shows experimental data for the polymer-solvent systems [15-17]. For polystyrene in benzene (PSB), in bromobenzene (PSBB),

TABLE 2. Computer Results of the Short-Range Interaction Parameter K_θ and of the Excluded Volume Parameter B for Polymer-Solvent Systems According to Different Equations

Serial number	System	Equation	K_θ (cm ³ /g)	$B \cdot 10^{27}$ (cm ³ /g)
1	Polystyrene-benzene	3	0.092	1.24
		4	0.088	2.20
		5	0.097	1.40
		7	0.070	4.92
		12	-	11.14
2	Polystyrene-bromobenzene	3	0.094	1.17
		4	0.090	2.08
		5	0.110	1.08
		7	0.071	4.28
		12	-	7.91
3	Polyacrylamide-0.2 M sodium chloride	3	0.226	1.01
		4	0.215	1.80
		5	0.202	1.51
		7	1.548	1.015
		12	-	1.92
4	Poly(D- β -Hydroxybutyrate)-trifluoroethanol	3	0.218	0.35
		4	0.201	1.18
		5	0.382	3.30
		7	0.265	11.78
		12	-	5.8

for polyacrylamide in 0.2 M aqueous sodium chloride solution (PAASC), and for poly(D- β -hydroxybutyrate) in trifluoroethanol (PHB), the \bar{M}_w and A_2 have been obtained at 20°C from sedimentation equilibrium experiments, and for PHB samples the data were collected from Ref. 17. The polyacrylamide samples are highly polydisperse as compared to polystyrene samples. The polymolecularity correction factors, namely q_{MH} and q_M , were calculated using Eqs. (6) and (13), respectively, and these data are reported in Table 1. For the calculation of q_{MH} , the Mark-Houwink exponents a were taken from an earlier study [15, 16] in which the following empirical relations were used:

$$[\eta] = 1.23 \times 10^{-2} \bar{M}_w^{0.72} \quad \text{for PSB system}$$

$$[\eta] = 1.19 \times 10^{-2} \bar{M}_w^{0.72} \quad \text{for PSBB system}$$

$$[\eta] = 3.02 \times 10^{-2} \bar{M}_w^{0.68} \quad \text{for PAASC system}$$

Using Eqs. (3), (4), (5), (7), and (12), the values of the parameters K_θ and B were calculated using a multiparametric curve fitting program on an IBM 4341 computer at Clarkson College. This program uses a nonlinear least squares analysis in conjunction with the method of steepest descent to vary the unknown parameters simultaneously until the best fit is achieved. The computed parameters for all the polymer-solvent systems using different equations are presented in Table 2.

As an example of a rather flexible polymer, we have selected poly(D- β -hydroxybutyrate), and the data of Akita et al. [17] have been fitted to the above relations with the estimated parameters presented in Table 2. From the computed values of K_θ it is quite obvious that quite identical results were obtained for polymers in good solvents, namely, PSB and PSBB systems; also, different procedures yielded identical results for all the systems. However, no systematic trend was observed for the excluded volume parameter B . It should be noted that even the Stockmayer-Fixman relation yields reasonably acceptable values of K_θ . In all the systems, Eqs. (7) and (12) generally yielded somewhat higher values for the parameter B compared to Eqs. (3) and (4). An exception to this was the PAA system where the estimated value for B from Eq. (12) was very small compared to the other three systems. Such a behavior was also observed in the data of Chiantore et al. [12] and for several other polymer-solvent systems [2]. This difference may be due to the error that is simultaneously accumulated from a combination of two sets of experimental data, thus magnifying the computed errors from Eq. (12).

In conclusion, it should be noted that all these procedures [1-10] are based on the extrapolation of experimental data to vanishing

molecular weight. However, as was pointed out by Flory [18], many assumptions of the perturbation theory are violated in the region of low molecular weight. Any extrapolation into that region may therefore yield widely distorted results. Quite recently, Munk and co-workers [19, 20] have offered semiempirical theoretical relations to treat the viscosity and molecular weight data for polymer-solvent systems. This procedure seems to be the best and is recommended for the evaluation of K_θ for any polymer-solvent system.

CONCLUSIONS

Analysis of the data from the relations proposed by Chiantore et al. indicates that the method is reasonably good for the evaluations of K_θ and B for polymer-solvent systems. At any rate, the data are not extensive enough to warrant deeper analysis, but we still believe that the method will satisfactorily serve to estimate K_θ and B of those polymers for which direct measurement is not possible.

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Note Added in Proof. In order to apply such a procedure to the experimental data of Table 1, one must account for the polydispersity of the polymer samples so the A_2 in Eq. (7) must be replaced by A_2^*/q_w , where q_w (see Eq. 13) is a polydispersity correction factor such that the quantity (A_2^*/q_w) represents the second virial coefficient of a monodisperse polymer sample having molecular weight equal to \bar{M}_w .