

Huggins' Constant and Unperturbed Parameter of Dilute Polymer Solutions

K. K. CHEE, *Department of Chemistry, University of Malaya, Kuala Lumpur 22-11, Malaysia*

Synopsis

A novel method developed to evaluate the unperturbed parameter K_θ from the viscometric data of dilute polymer solutions can be considerably simplified by making the reasonable assumption that the Huggins' constant under theta conditions, $k_{H\theta}$, is equal to $1/2$ for a number-average degree of polymerization of over about 2000. Two linear equations are derived pertaining to the present analysis, one to deal with the experimental data, and the other specially to estimate the intrinsic viscosity $[\eta]_\theta$ which corresponds to $k_{H\theta}$. All calculations were done by the linear least-squares method. The K_θ was computed by the Mark-Houwink-Sakurada equation. It is shown that reliable results on K_θ can be obtained for polystyrene and poly(vinyl acetate).

INTRODUCTION

The Huggins' equation was first derived in 1942 to deal with the concentration dependence of the zero-shear viscosity η of dilute polymer solutions.¹ It is always expressed in the following form by which the intrinsic viscosity $[\eta]$ as well as the Huggins' constant k_H can be evaluated conveniently:

$$(\eta\eta_0^{-1} - 1)C^{-1} = [\eta] + k_H[\eta]^2C \quad (1)$$

where η_0 and C are the solvent viscosity and the polymer concentration, respectively. Equation (1) shows that a plot of the *lhs* against C would give $[\eta]$ from the intercept at $C = 0$ and the $k_H[\eta]^2$ from the slope of the straight line.

The size of the polymer in terms of the viscosity-average molecular weight \bar{M}_v may be empirically estimated from the intrinsic viscosity by using the Mark-Houwink-Sakurada (MHS) equation. Under theta conditions, this equation gives the corresponding intrinsic viscosity $[\eta]_\theta$ as

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

where K_θ is the unperturbed parameter which, in turn, is connected with the unperturbed dimensions of the polymer via the well-known Flory-Fox equation.²

Eirich et al.³ and others⁴ have reported that the slope $k_H[\eta]^2$ is actually a linear function in $[\eta]$, i.e.,

$$k_H[\eta]^2 = A + B[\eta] \quad (3)$$

where A and B are two empirical constants for a particular polymer sample at a constant temperature. This relationship was later theoretically substantiated by Bhatnagar and co-workers⁵ who further demonstrated that

$$A = -B^2/2 \quad (4)$$

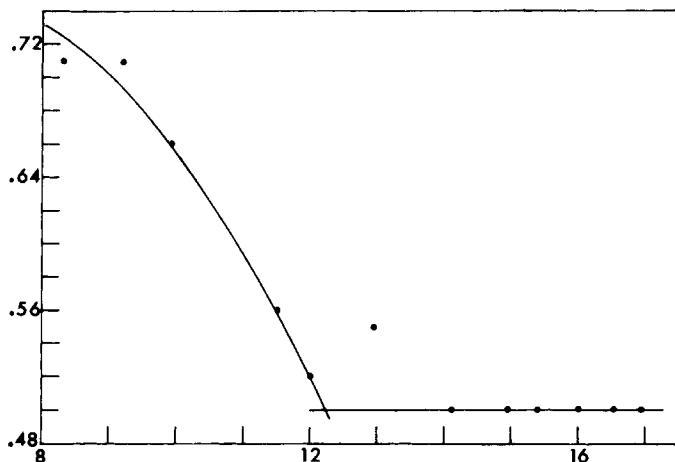


Fig. 1. Plot of $k_{H\theta}$ vs. $\ln \bar{M}_w$ for polystyrene under theta conditions.

Over the past few decades, theoretical considerations of k_H have been performed on solute particles of different shapes.⁶ However, these results, including those for the random coil polymers in the theta states, are amply inconsistent.⁷ Moreover, this interaction parameter k_H is more than a simple factor which depends on the goodness of solvent only, for it also varies with the shear rate, the molecular weight, and the degree of branching.^{8a} In view of these unfortunate situations we have to rely upon the empirical relations established from reliable sources.

Einaga, Miyaki, and Fujita⁹ have provided the values of $[\eta]_\theta$ and $k_{H\theta}$ for the dilute solutions of polystyrene fractions in cyclohexane at 34.5°C, covering the weight-average molecular weights \bar{M}_w over a broad range from 1×10^3 to 6×10^7 , where $k_{H\theta}$ refers to k_H under theta conditions. Figure 1 displays these results by plotting the $k_{H\theta}$ as a function of $\ln \bar{M}_w$ under these theta conditions. Obviously, $k_{H\theta}$ decreases as \bar{M}_w increases to a certain limit (which is equal to $\bar{M}_w = 2.1 \times 10^5$ in this particular case), beyond which the $k_{H\theta}$ is equal to 0.5 and is insensitive to the \bar{M}_w . Incidentally, this constant value coincides with the prediction of the Yamahawa theory of polymer solutions.¹⁰ In this work, Figure 1 is used to obtain the value of $k_{H\theta}$ at any \bar{M}_w .

Recently, we have proposed two novel methods to evaluate K_θ from viscometric data.^{11,12} This article reports another simple procedure to assess the K_θ as explained below.

Apparently, once $k_{H\theta}$ is known from the standard curve in Figure 1, $[\eta]_\theta$ may be computed by using eq. (3) if A and B are predetermined. However, because of the quadratic nature of this equation, a solution for $[\eta]$ at $k_{H\theta}$ is not possible if $k_{H\theta} > k_{HC}$, where

$$k_{HC} = -B^2/4A \quad (5)$$

It is shown later that this may happen in many instances, particularly for high-molecular-weight polymer fractions. In order to overcome this difficulty, we expand eq. (3) in a Taylor series for $[\eta]$, about a reference k_H denoted by k'_H , and retain only the first two terms to get a linear expression in k_H :

$$[\eta] = a + bk_H \quad (6)$$

where

$$a = B(k'_H)^{-1} + (B^2 + 4Ak'_H)^{1/2}(k'_H)^{-1} - A(B^2 + 4Ak'_H)^{-1/2} \quad (6a)$$

$$b = [a - A(B^2 + 4Ak'_H)^{-1/2}](2k'_H)^{-1} \quad (6b)$$

It follows that eq. (6) may be used to compute $[\eta]_\theta$, which then yields K_θ by eq. (2).

RESULTS AND DISCUSSION

Munk et al.¹³ have studied the viscometric behavior of a number of polystyrene samples in benzene, cyclohexane, ethyl acetate, and their mixed solvent pairs at 20°C. All these samples are well characterized and have their weight-average-to-number-average molecular weight ratios \bar{M}_w/\bar{M}_n less than 1.15 in any case. Some of their work is employed for the present purposes to produce the results summarized in Table I.

Polystyrene sample 1c of molecular weight 1.77×10^5 has been extensively studied and therefore is chosen to illustrate this procedure. First of all, data on $[\eta]$ and k_H from different solvents are collected and fitted to eq. (3) using the linear least-squares method. In this case, the total population of variables N is equal to 30, and the lowest and highest limits of k_H are 0.341 and 0.500, respectively. The results for the constants A and B and for the linear correlation coefficient r are cited in Table I. The coefficient r is found to be 0.9744, a value that adequately satisfies the linear relation (3) as well as the least-squares line drawn in Figure 2(a). However, attempts to calculate the $[\eta]_\theta$ directly from eq. (3) were unsuccessful, since the values of $k_{H\theta}$ and k_{HC} as derived from Figure

TABLE I
Values of Statistical and Unperturbed Parameters for Polystyrene and Poly(vinyl Acetate)

Parameter	Polystyrene				Poly(vinyl acetate)
	Sample 13a (6.19×10^5) ^a	3b (3.79×10^5)	1c (1.77×10^5)	4b (1.13×10^5)	1B (2.17×10^5) (\bar{M}_n)
	Analysis of Eq. (3)				
A (ml/g) ²	-3306	-1886	-623.8	-208.4	-1222
B (ml/g)	77.7	59.8	34.7	23.6	46.9
r	0.9958	0.9929	0.9744	0.9785	0.9781
Lowest k_H	0.338	0.345	0.341	0.377	0.280
Highest k_H	0.507	0.475	0.500	0.578	0.560
N	11	11	30	11	5
	Analysis of Eq. (6)				
a (ml/g)	404.1	302.7	172.3	—	244.0
b (ml/g)	-682	-495	-276	—	-415
r	-0.9997	-0.9994	-0.9992	—	-0.9996
Lowest k_H	0.330	0.330	0.330	—	0.330
Highest k_H	0.450	0.470	0.470	—	0.420
k'_H	0.367	0.375	0.385	—	0.368
	Results				
$k_{H\theta}$	0.500	0.500	0.512	0.550	0.500
$[\eta]_\theta$ (ml/g)	63.1	55.2	31.0	30.5	36.5
K_θ (ml/g)	0.080	0.090	0.074	0.091	0.078

^a The designations used in the original report are followed here; figures in parentheses are molecular weights.

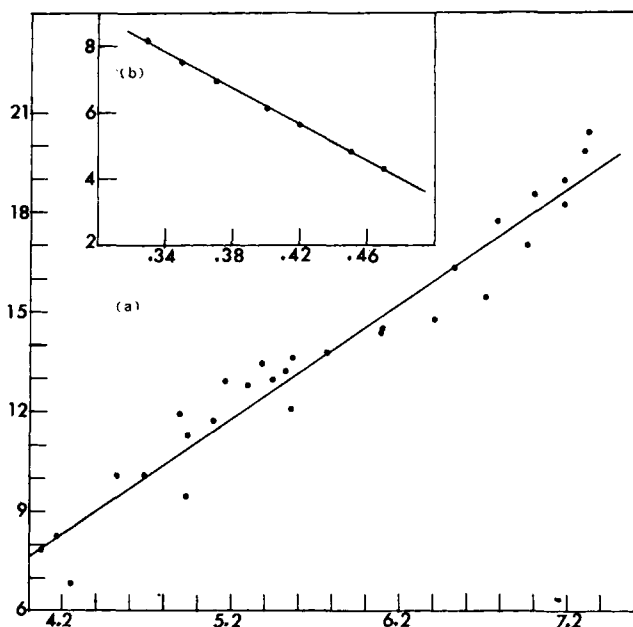


Fig. 2. (a) Plot of eq. (3) with $k_H[\eta]^2 \times 10^{-2}$ (ml/g)² vs. $[\eta] \times 10^{-1}$ (ml/g) for polystyrene sample 1c at 20°C. (b) Plot of eq. (6) with $[\eta] \times 10^{-1}$ (ml/g) vs. k_H for the same sample.

1 and eq. (5), respectively, show that $k_{H\theta} > k_{HC}$. Thus, we resort to eq. (6) in this connection.

Figure 2(b) demonstrates a linear plot of eq. (6) for sample 1c. Here, the data points are calculated from eq. (3) based on the values of A and B determined previously. Again, the linear least-squares technique is employed to compute the values of a and b listed in Table I. The coefficient r , which has a value close to unity, supports this truncated Taylor series about $k'_H = 0.385$, obtained from eq. 6(b), for $0.330 \leq k_H \leq 0.470$. Finally, eq. (6) results in $[\eta] = 31.0$ ml/g at $k_{H\theta} = 0.512$ (from Fig. 1); and it follows from eq. (2) that K_θ is 0.074 ml/g. All are listed in Table I.

The two independent variables in Figures 2(a) and 2(b) are $[\eta]$ and k_H , respectively. It is noted that the experimental errors involved in these two parameters are usually $\Delta k_H/k_H > 3\%$ at least and $\Delta[\eta]/[\eta] < 1\%$ at most.¹¹

This would allow us to estimate the corresponding percent errors in the ordinates. A simple error analysis of eqs. (3) and (6) respectively results in

$$\frac{\Delta(k_H[\eta]^2)}{(k_H[\eta]^2)} = B(k_H[\eta])^{-1} \frac{\Delta[\eta]}{[\eta]} \quad (7)$$

$$\frac{\Delta[\eta]}{[\eta]} = |b|(k_H/[\eta]) \frac{\Delta k_H}{k_H} \quad (8)$$

Consequently, the percent error of $\Delta[\eta]/[\eta]$ is at least about three times that of $\Delta(k_H[\eta]^2)/(k_H[\eta]^2)$ at $k_H = 0.330$, and these deviations become increasingly severe as the values of k_H further increase. These findings indicate that the experimental data are better fitted to eq. (3) than to eq. (6). This explains that eq. (6) is not meant for the raw data on $[\eta]$ and k_H but rather is an approximate

version of eq. (3) devised to facilitate the estimation of $[\eta]$ at an otherwise inaccessible $k_{H\theta}$ in eq. (3).

For sample 1b, which has the lowest molecular weight (1.13×10^5 in Table I), k_{HC} is less than $k_{H\theta}$ and does not need eq. (6). At this low molecular weight, Figure 1 gives $k_{H\theta} = 0.550$, which leads to $K_\theta = 0.091$ ml/g via eqs. (2) and (3). The other two polystyrene fractions are of high molecular weights well above the critical molecular weight shown in Figure 1. Thus, we take $k_{H\theta} = 0.500$ for both samples 13a and 3b to get $K_\theta = 0.080$ and 0.090 ml/g, respectively. Though the K_θ values for polystyrene in Table I seem to be scattered, they are comparable with the literature values, which spread from 0.070 to 0.090 ml/g.^{8b,9,11} The average value of K_θ is 0.084 ml/g at 20°C . Details of statistical analyses are included in Table I.

The viscosities of dilute solutions of linear poly(vinyl acetate) have been investigated by Moore and Murphy¹⁴ at various temperatures and solvents. One of these fractionated samples, code 1B, of number-average molecular weight \bar{M}_n marginally exceeding the critical molecular weight in Figure 1, is particularly of interest to us. The polymer solutions were prepared at 25°C using acetone, chloroform, chlorobenzene, dioxane, and methanol as solvents. Equations (3) and (6) were applied to acquire the results contained in Table I. The K_θ so obtained for the poly(vinyl acetate) at 25°C was 0.078 ml/g, which is in good agreement with the reported figures.^{8b} The usual technique produced $K_\theta = 0.078$ ml/g in 6-methyl-3-heptanone at 66°C and $K_\theta = 0.082$ ml/g in 3-heptanone at 26.8°C .

Figure 3 confirms the relation (4), since the straight line *E* drawn to fit the data points is close to the theoretical line *T* of gradient equal to unity. The difference between them is about 10%. This implies that eq. (3) is theoretically and empirically justifiable.

This work is solidly based on the empirical relation between $k_{H\theta}$ and the mo-

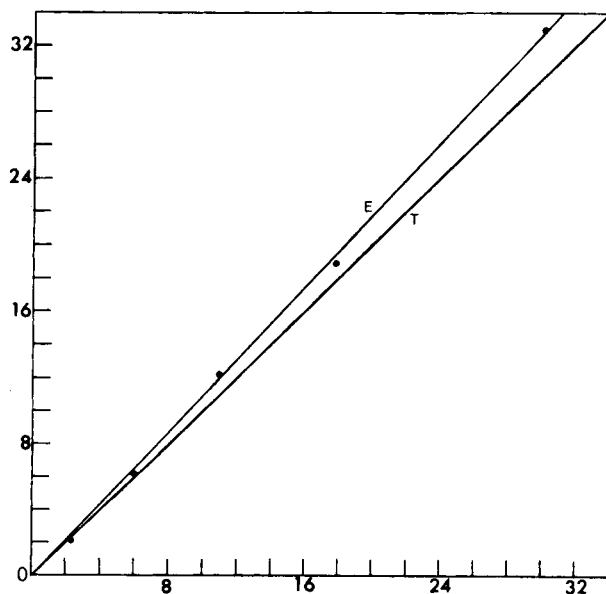


Fig. 3. Test plot for relation (4) with $-A \times 10^{-2} (\text{ml/g})^2$ vs. $(B^2/2) \times 10^{-2} (\text{ml/g})^2$.

lecular weight (Fig. 1) and also eq. (3). However, for polymers of sufficiently high molecular weight, probably over 2.1×10^5 , we may assume $k_{H\theta} = 0.500$, as suggested by Figure 1. In comparison with the conventional method for K_θ , which requires a series of polymer samples, we find that the present procedure is relatively simple and more flexible in that (1) it may need only one polymer sample, (2) the theta solvent may not be known, and (3) it virtually can be operated at any constant temperature, provided that a wide spectrum of solvents is available. Mixed solvents of various solvent power are equally workable.

References

1. M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).
2. P. J. Flory and T. G. Fox Jr., *J. Am. Chem. Soc.*, **73**, 1904 (1951).
3. F. Eirich and J. Riseman, *J. Polym. Sci.*, **4**, 417 (1949).
4. D. J. Streeter and R. F. Boyer, *Ind. Eng. Chem.*, **43**, 1790 (1951).
5. H. L. Bhatnagar, A. B. Biswas, and M. K. Gharpurey, *J. Chem. Phys.*, **28**, 88 (1958).
6. H. L. Frisch and R. Simha, in *Rheology*, Vol. 1, F. R. Eirich, Ed., Academic, New York, 1956, Chap. 14.
7. F. A. H. Peeters and A. J. Staverman, *Macromolecules*, **10**, 1164 (1977).
8. (a) N. Sutterlin, Chap. IV, p. 135; (b) M. Kurata, Y. Tsunashima, M. Iwama, and K. Kamada, Chap. IV, p. 1; in *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., Interscience, New York, 1975.
9. Y. Einaga, Y. Miyaki, and H. Fujita, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 2103 (1979).
10. H. Yamakawa, *J. Chem. Phys.*, **34**, 1360 (1961).
11. K. K. Chee, *Eur. Polym. J.*, **16**, 15 (1980).
12. K. K. Chee, *J. Appl. Polym. Sci.*, **26**, 4299 (1981).
13. P. Munk, M. T. Abijaoude, and M. E. Halbrook, *J. Polym. Sci. Polym. Phys. Ed.*, **16**, 105 (1978).
14. W. R. Moore and M. Murphy, *J. Polym. Sci.*, **56**, 519 (1962).

Received September 17, 1981

Accepted October 30, 1981