On the excluded volume theories: fifth-power type equations

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Two new equations, based on the Domb–Barrett and Kurata theories of excluded volume, have been proposed to estimate unperturbed dimensions of chain molecules in solution from the viscosity–molecular weight data of polymers in good solvents. The fifth-power type equations of excluded volume theories by Domb and Barrett, Kurata, and Flory have been compared using the experimental data on several polymers. It has been found that the Domb–Barrett theory not only reliably yields the unperturbed dimensions of polymers but also adequately measures the solvent–polymer interaction parameter.

Since the introduction of the concept of excluded volume (long range intramolecular interactions) in dilute polymer solutions by Flory[1], a number of attempts have been made to describe this characteristic effect of linear flexible chain molecules within the frame work of the two parameter theory. All the theories correlate the expansion factor (α) of a polymer chain with the excluded volume parameter (z) leading to the asymptotic form:

$$\lim_{z\to\infty} \alpha^x = \text{constant } z \tag{1}$$

where x is a constant independent of z. Several values between 1 and 6.67 for x have been predicted as reviewed by Yamakawa[2]. The examination of an asymptotic solution of α at large z based on the self-consistent field approach, and the exact enumeration of non-intersecting walks in three-dimensional lattices, as discussed by Yamakawa[2], consider the fifth-power ($x = 5$) type equations fairly satisfactory in describing the behaviour of α over the range of z experimentally accessible.

Very recently Domb and Barrett[3] have proposed a new formula correlating α and z within the framework of the two parameter theory. Their approach is based on critical point thermodynamics. By combining the exact enumeration data on non-intersecting walks on three-dimensional lattices with the virial expansion they arrived at the following formula:

$$\alpha^{10} = 1 + \frac{20}{3}z + 4\pi z^2 \tag{2}$$

with

$$\alpha^2 = \langle R^2\rangle/\langle R^2\rangle_0$$

$$z = \left(\frac{3}{2\pi a^2}\right)^{3/2} \beta n^{1/2}$$

where $\langle R^2\rangle$ and $\langle R^2\rangle_0$ are the mean square end-to-end distances of a polymer chain in perturbed (with excluded volume effect) and unperturbed (zero excluded volume, i.e. at θ-conditions) states, respectively, a is the effective bond length, n is the number of bonds in a chain molecule and β is the binary cluster integral having the dimension of volume. Equation (2) is a fifth-power type equation. The aim of the present communication is to test equation (2) with the experimental data and compare with other fifth-power type equations.

The intrinsic viscosity $[\eta]$ may be expressed in the form:

$$[\eta] = KM^{1/2}\alpha_\eta^3 \tag{3}$$

with

$$K = \Phi_0 A^3 \tag{4}$$

$$A^2 = \langle R^2\rangle_0/M \tag{5}$$

where Φ_0 is the universal constant, K is the measure of unperturbed dimensions of the chains of molecular weight M, and α_η is the expansion factor derived from viscosity measurements. For convenience we rewrite the excluded parameter z as follows:

$$z = 0.33\Phi_0 BM^{1/2}/K \tag{6}$$

where B is the solvent–polymer interaction parameter.

The factor α_η must become unity as the molecular weight tends to zero, for $\alpha_\eta = 1$ at $z = 0$. The excluded volume effect, therefore, decreases with decreasing molecular weight. This suggests that the value of K may be obtained by extrapolation to zero molecular weight from viscosity data in good solvents. We assume that $\alpha = \alpha_\eta$ and this does not lead to any error in the comparison of the theories.

The Domb–Barrett relation, equation (2), is a quadratic equation in z. The plausible solution of this quadratic equation leads to the following relation:

$$4\pi z + \frac{20}{3} = 3.33 + [11.1 + 12.56(\alpha^{10} - 1)]^{1/2} = g_1(\alpha) \tag{7}$$

Now, the Domb–Barrett relation reads as follows:

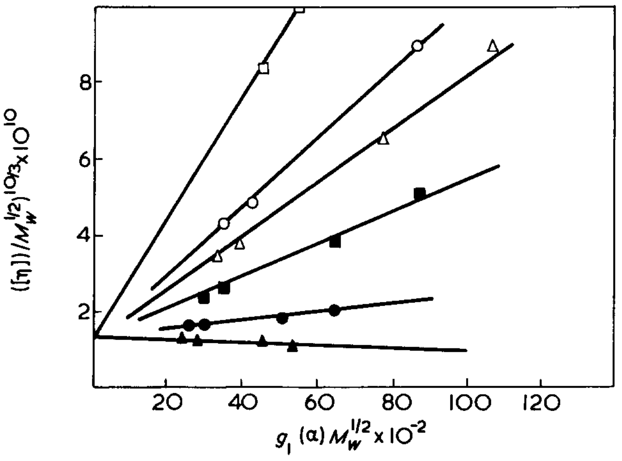

Figure 1 The Domb–Barrett plots, from equation (9), for sodium amylose sulphate[6] in aqueous NaCl solutions of molarity: □, 0.04 M (ν = 0.77); ○, 0.08 M (ν = 0.69); △, 0.10 M (ν = 0.67); ■, 0.15 M (ν = 0.62); ●, 0.30 M (ν = 0.54); ▲, 0.50 M (ν = 0.50), at 33°C

$$\alpha^{10} = 1 + zg_1(\alpha) \tag{8}$$

which on combination with equations (3) and (6) yields:

$$\left(\frac{[\eta]}{M^{1/2}}\right)^{10/3} = K^{10/3} + 0.33\Phi_0 BK^{7/3}\,[g_1(\alpha)M^{1/2}] \tag{9}$$

Similarly, the Kurata theory[4] of excluded volume:

$$\frac{1}{5}(\alpha^5 - 1) + \frac{1}{3}(\alpha^3 - 1) = \frac{4}{3}z \tag{10}$$

may be rearranged as given below:

$$\alpha^3(3\alpha^2 + 5)/8 = 1 + 2.5z \tag{11}$$

On combining equation (11) with equations (3) and (6), we obtain:

$$\frac{[\eta]}{M^{1/2}}\,g_2(\alpha) = K + 0.825\Phi_0 BM^{1/2} \tag{12}$$

with

$$g_2(\alpha) = (3\alpha^2 + 5)/8 \tag{13}$$

The well known Flory–Fox–Schaefgen relation[5] derived from Flory's excluded volume theory[1]:

$$\alpha^5 - \alpha^3 = 2.60z \tag{14}$$

is given by:

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K^{2/3} + 0.858K^{2/3}\Phi_0 B\,\frac{M}{[\eta]} \tag{15}$$

Equations (2), (10) and (14) are fifth-power type due to Domb and Barrett[3], Kurata[4] and Flory[1], and the corresponding $[\eta] - M$ relations are given by equations (9), (12) and (15). According to equation (9), a plot of $([\eta]/M^{1/2})^{10/3}$ against $g_1(\alpha)M^{1/2}$ should be linear and yield an intercept equal to $K^{10/3}$ which is a measure of unperturbed dimensions of the polymer chains in solution. First $([\eta]/M^{1/2})^{10/3}$ against $6.66\,M^{1/2}$ [since $g_1(\alpha) = 6.66$ for $\alpha = 1$] is plotted to find a first order approximate value of K, and then replotted $([\eta]/M^{1/2})^{10/3}$ against $g_1(\alpha)M^{1/2}$, where $g_1(\alpha)$ is calculated from equations (3) and (7) with the first order value of K. The process of plotting is repeated till a constant value of K is obtained. Similarly, following the iteration method, $[\eta]\,g_2(\alpha)/M^{1/2}$ against $M^{1/2}$ is plotted according to equation (12) to estimate the unperturbed dimensions.

The viscosity–molecular weight data[6] on sodium amylose sulphate in aqueous solutions with added simple salt, NaCl, at 33°C are used to determine the molecular dimensions of the chains in the unperturbed state applying three of the fifth-power type equations. It is noted that sodium amylose sulphate in the presence of a sufficient amount of added salt behaves like a non-ionic polymer in solution. Further, we consider $[\eta] - M$ data such that $\nu < 0.8$ (in $[\eta] = KM^\nu$) since the upper limit of validity of the fifth-power type equations is $\nu = 0.8$.

Figures 1–3 show the plots due to equations (9), (12) and (15) respectively, for sodium amylose sulphate in aqueous salt solutions at 33°C. The concentration range 0.04–0.30 M of NaCl solution is considered to show the effect of solvent power on the plots. The corresponding range of ν covered is 0.77–0.50. All solvent lines in *Figure 1* are linear plots giving a common intercept on the ordinate, and this is in excellent agreement with the results of the θ-experiment. Again linear plots are observed in

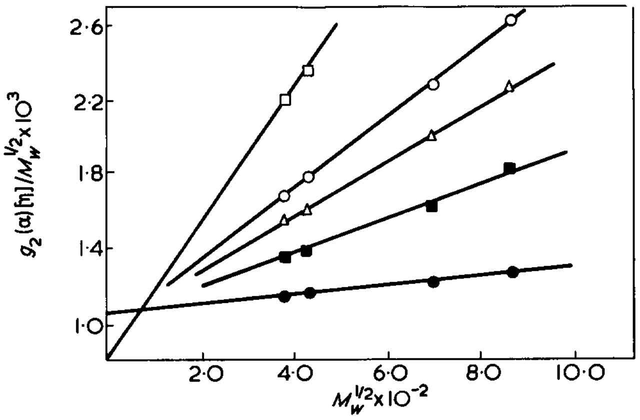

Figure 2 The Kurata plots, from equation (12), for the data in *Figure 1*

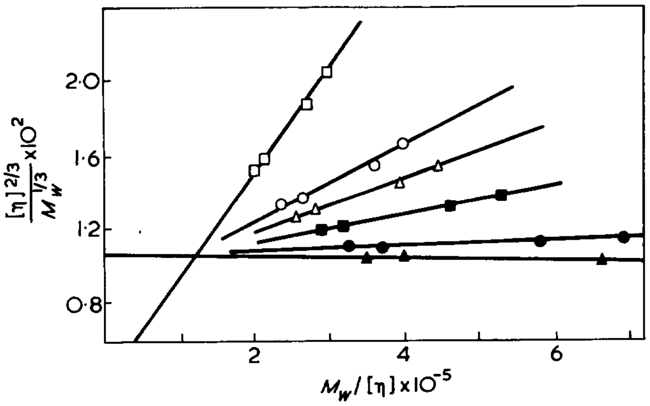

Figure 3 The Flory–Fox–Schaefgen plots, from equation (15), for the data in *Figure 1*

Table 1 The values of solvent–polymer interaction parameter ($B \times 10^{27}$ cm^3) for sodium amylose sulphate in aqueous sodium chloride solutions of different concentration at 33°C

	NaCl solutions (M)			
	0.04	0.08	0.15	0.30
Equation (9)	1.42	0.79	0.40	0.12
Equation (12)	1.54	0.81	0.39	0.11
Equation (15)	6.19	1.09	0.19	0.06
SF*	1.44	0.82	0.38	0.10

*Stockmayer–Fixman theory[12]

Figures 2 and *3* but the common intercept on the ordinate is not observed in either case. However, the common point of intersection is observed in both cases as noted previously[7]. It may be said that in good solvents the solvent–polymer interaction is over-estimated and hence equations (12) and (15) may not yield reliable unperturbed dimensions, particularly from the viscosity data in good solvents. The comparison of the Figures, beyond any doubt, establishes the superiority of equation (9) among the fifth-power type equations. The analysis of the data on several other polymers: sodium carboxymethyl amylose[8], amylose tripropionate[9], isotactic poly(butene-1)[10], and poly(*m*-methylstyrene)[11], supports the above observations.

On the other hand, we evaluate the solvent–polymer interaction parameter B from the slope of lines in *Figures 1–3*; Φ_0 being 2.87×10^{23} cgs. The values of B are tabulated in *Table 1*. In addition, *Table 1* lists the values of B obtained from the data on sodium amylose sulphate according to the Stockmayer–Fixman (SF)[12] theory which is based on the Fixman's excluded volume theory[13] (third-power type equation). Yamakawa[2] has shown that the estimate of B from SF theory is comparable with that derived from light scattering measurements. The Table reveals that B values derived from equation (15), i.e. from the slope of lines in *Figure 3*, are much higher in good solvents and lower in poor solvents than that derived from the rest of the equations. The B values derived from equations (9) and (12) compare satisfactorily with that from the SF theory in all solvents.

Thus, in view of the determination of unperturbed dimensions of polymer chains and solvent–polymer interactions, the Domb–Barrett equation seems most promising. The Kurata theory estimates reliable solvent–polymer interactions, although the estimated unperturbed dimensions are only approximate. The Flory theory in its original form is quite unsatisfactory for both the parameters as observed by others[2,14]. It seems from the present analysis that the theories based on the assumed form of the binary cluster integral are inferior to the theory based on more realistic enumeration data on non-intersecting walks and the virial expansion.

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