

Linear representation of viscosity data as a function of molecular weight

Anastasios Dondos and Henri Benoit

Centre de Recherches sur les Macromolécules (CNRS), 6, rue Boussingault, 67083 Strasbourg Cedex, France

(Received 29 December 1977)

A correction of the Stockmayer–Fixman–Burchard equation is proposed using one additional parameter. This parameter is linearly related to the a coefficient of the Mark–Houwink–Sakurada equation and its use gives a linear plot for viscosity over a very broad range of molecular weights.

INTRODUCTION

In two recent papers^{1,2} we described a new plot of intrinsic viscosity as a function of molecular weight which gives a straight line, especially in the range of the low molecular weights where the a exponent of the Mark–Houwink–Sakurada equation $[\eta] = KM^a$ is not a constant. This relation has been also applied successfully to polymers dissolved in a two component solvent system³.

In all cases there is a deviation from linearity for very large molecular weights. Even with this limitation this plot is more advantageous than the classical Stockmayer–Fixman–Burchard plot^{4,5}, which is linear, especially in good solvents, over a rather narrow range of molecular weights.

In this paper we will show that by introducing a small correction term depending on only one parameter it is possible to obtain a linear plot for all accessible molecular weights. Moreover it will be shown that this new parameter is a smooth function of the exponent a of the Mark–Houwink–Sakurada equation.

EMPIRICAL EQUATION

In the preceding paper² we started from the following equation:

$$\frac{1}{[\eta]_\theta} - \frac{1}{[\eta]} = A_2 + \frac{A'}{M^{1/2}} \quad (1)$$

Writing $[\eta]_\theta = K_\theta M^{1/2}$ and $A_1 = (1/K_\theta) - A'$ we obtained the relation:

$$\frac{1}{[\eta]} = -A_2 + \frac{A_1}{M^{1/2}} \quad (2)$$

Plotting $[\eta]^{-1}$ as a function of $M^{-1/2}$ good linear behaviour is obtained. However, this plot does not allow us to check the validity of equation (2) for large molecular weights.

If equation (1) is used, plotting $\{[\eta]_\theta^{-1} - [\eta]^{-1}\}M^{1/2}$ as a function of $M^{1/2}$, we should also obtain a straight line if equations (1) and (2) are valid.

In fact, as can be seen in ref 1, there is a downward curvature for high molecular weights; the experimental values are lower than predicted. The distance from the

straight line increases almost linearly with molecular weight. This suggests the introduction of a small correction term DM , writing:

$$\left\{ \frac{1}{[\eta]_\theta} - \frac{1}{[\eta]} \right\} M^{1/2} = A_2(1 - DM) + A' \quad (3)$$

This procedure is valid as long as DM is small compared to unity. For very large M other terms should be introduced or the variation of D as a function of M should be taken into account.

Assuming that equation (3) is valid, one can write an extension of equation (2):

$$\frac{1}{[\eta]} = -A_2(1 - DM^{1/2}) + \frac{A_1}{M^{1/2}} \quad (4)$$

This extra term does not affect the results obtained for low molecular weights but drastically changes the behaviour for large M .

It is interesting to compare equation (4) with the Stockmayer–Fixman–Burchard equation^{4,5}.

$$\frac{[\eta]}{M^{1/2}} = K_\theta + 0.51 \phi_0 BM^{1/2} \quad (5)$$

Assuming that,

$$A_1 \gg A_2 M^{1/2} (1 - DM^{1/2})$$

which, as it will be shown later, is practically always justified one obtains from equation (4):

$$\frac{[\eta]}{M^{1/2}} = \frac{1}{A_1} + \frac{A_2}{A_1^2} M^{1/2} (1 - DM^{1/2}) + \dots \quad (6)$$

Neglecting the higher terms we obtain a corrected Stockmayer–Fixman–Burchard equation differing from the original through the term $1 - DM^{1/2}$.

EXPERIMENTAL VERIFICATIONS

As we have shown earlier² the determination of A_1 and A_2 is very easy when the intrinsic viscosity and the molecular

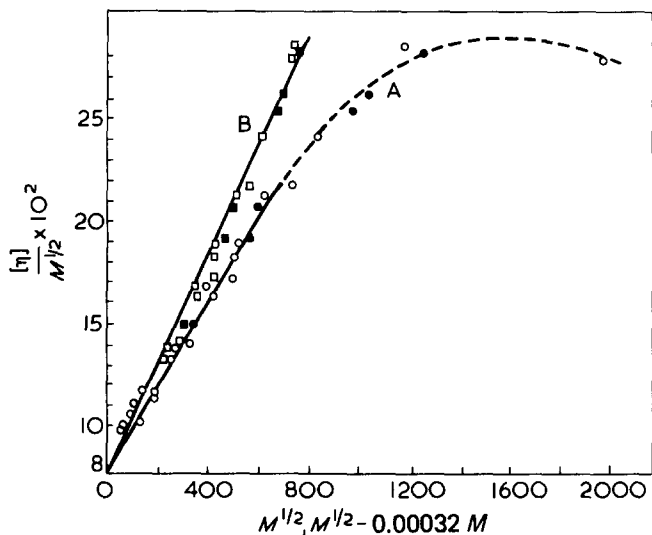


Figure 1 A, Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ and B, versus $M^{1/2} - 0.00032M$ for PS samples in CHCl_3 at 25°C : this work (\circ, \square); results from ref 6 (\bullet, \blacksquare)

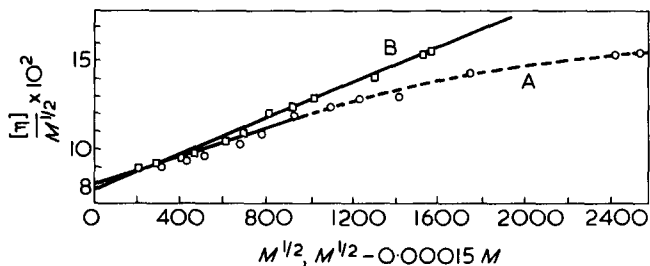


Figure 2 A, Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ and B, versus $M^{1/2} - 0.00015M$ for PS samples in methyl ethyl ketone at 35°C . Results from ref 7

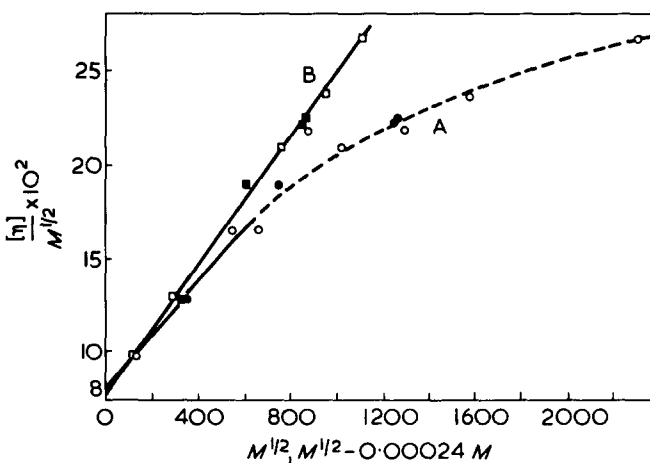


Figure 3 A, Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ and B, versus $M^{1/2} - 0.00024M$ for PS samples in dichloroethane. Results from ref 7 (\circ, \square), results from ref 8 (\bullet, \blacksquare)

weight of fractions of low molecular weights are known. The term $DM^{1/2}$ can be neglected and a straight line is obtained for a plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$. The term $DM^{1/2}$ represents the deviation from the straight line in the high molecular weight range. It is very easy to evaluate the value of D which gives the best fit between equation (6) and the experimental data. When the value of D is known we can

use the representation $[\eta]/M^{1/2}$ as a function of $M^{1/2} - DM$ which should give a straight line.

In Figures 1 to 6 we give the results for six different systems using the two representations: $[\eta]/M^{1/2}$ as a function of $M^{1/2}$ (equation 5) and $[\eta]/M^{1/2}$ as a function of $M^{1/2} - DM$ (equation 6).

Almost all results are taken from the literature and in each Figure we give the reference and the value of the D parameter. The values of $[\eta]$ are expressed in cm^3/g .

DISCUSSION AND CONCLUSIONS

A few authors¹³⁻¹⁵ have already tried to extend the domain of validity of the Stockmayer-Fixman-Burchard equation (5), using other values for the exponent of M instead of $1/2$.

From a practical point of view our representation seems to be more efficient. In all the data which have been present-

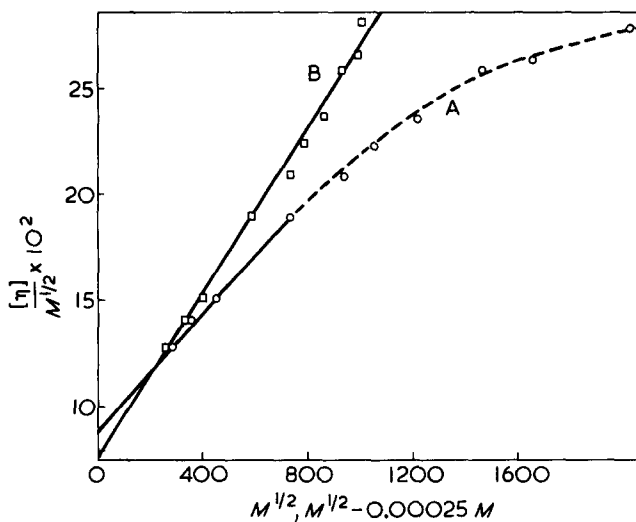


Figure 4 A, Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ and B, versus $M^{1/2} - 0.00025M$ for poly(α -methylstyrene) samples in toluene at 30°C . Results from ref 9

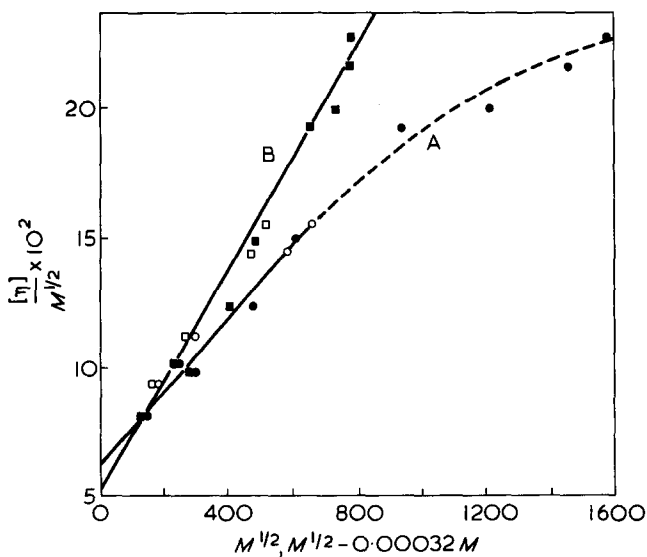


Figure 5 A, Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ and B, versus $M^{1/2} - 0.00032M$ for poly(methyl methacrylate) samples in benzene at 30°C . This work (\circ, \square); results from ref 10 (\bullet, \blacksquare)

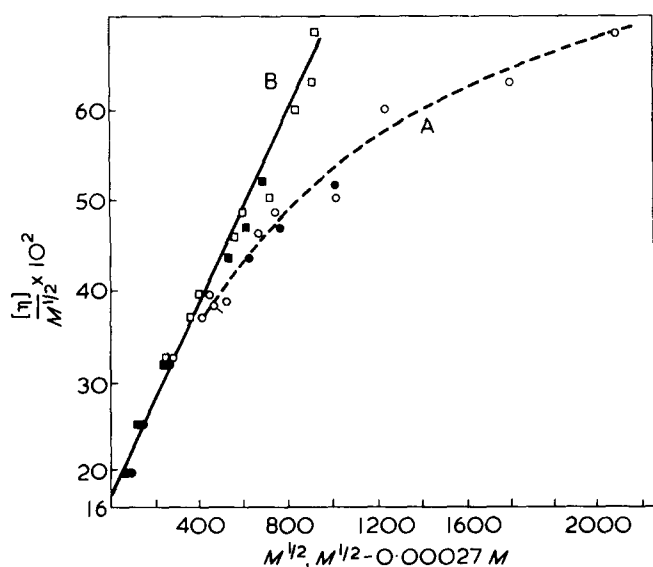


Figure 6 A, Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ and B, versus $M^{1/2} - 0.00027M$ for poly(ethylene oxide) samples in benzene at 25°C. Results from ref 11, (○) and from ref 12 (●)

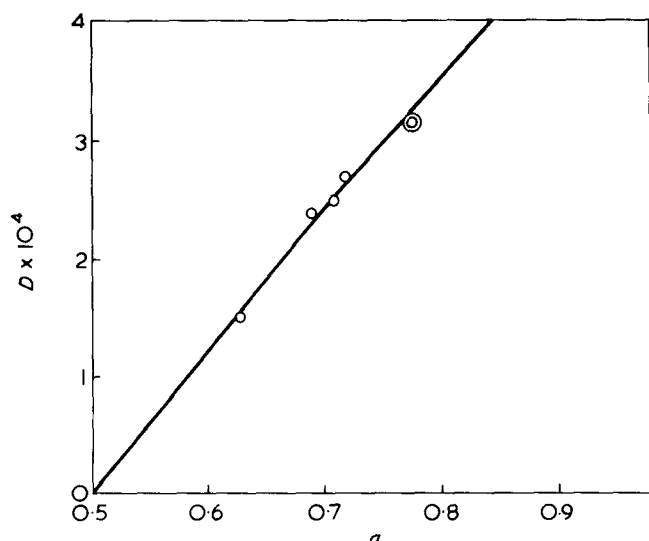


Figure 7 Parameter D as a function of Mark-Houwink-Sakurada coefficient a , for systems mentioned in Figure 1-6

ted the linear representation is valid from very low to very high molecular weights. We will try to see if a correlation can be established between D and some other characteristic parameter of the polymer-solvent system.

In Figure 7 we have plotted D as a function of the Mark-Houwink-Sakurada coefficient, a . Evidently, for $a = 0.5$ D has to be zero. But it is remarkable to see that there is practically a linear relationship between D and a giving the relation:

$$D = 12 \times 10^{-4}(a - 0.5) \quad (7)$$

As a check for the validity of this relation we have taken the system polystyrene-benzene at 30°C using the results of Yamamoto, Fujii, Tanaka and Yamakawa¹⁶. They give a value of 0.73 for a and a Stockmayer-Fixman-Burchard plot without any linear section (Figure 8). From equation (7) we evaluate $D = 0.000275$ and using our equation (6) we

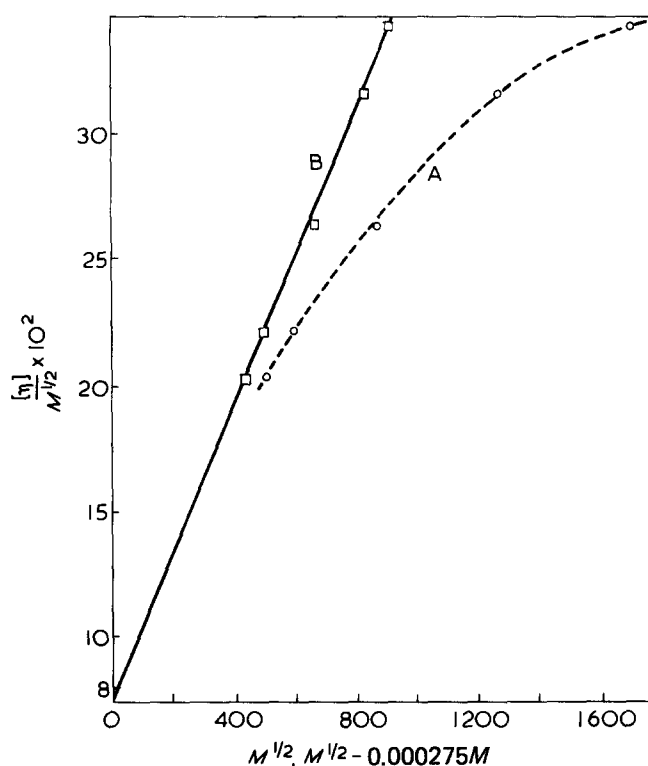


Figure 8 A, Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ and B, versus $M^{1/2} - 0.000275M$ for PS samples in benzene at 30°C. Results of ref 16

obtain the curve B of Figure 8. This curve is a very good straight line. Its extrapolation to $M = 0$ gives $K_{\theta} = 7.8 \times 10^{-2}$. This value is in very good agreement with the value obtained for PS by direct measurements in a θ solvent.

It should be noted that the correction we have introduced is limited to molecular weights for which $DM^{1/2}$ is lower than unity. Taking into account the numerical values of D this gives an upper limit of $M = 10^7$ above which equation (6) cannot be used. Therefore it is possible to use equation (2) for molecular weights lower than 300 000 and equation (6) for the whole range of practically accessible molecular weights.

REFERENCES

- 1 Dondos, A. *Eur. Polym. J.* 1977, **13**, 829
- 2 Dondos, A. and Benoit, H. *Polymer* 1977, **18**, 1161
- 3 Dondos, A. *Polymer* 1977, **18**, 1250
- 4 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci. (C)* 1963, **1**, 137
- 5 Burchard, W. *Makromol. Chem.* 1961, **50**, 20
- 6 Oth, J. and Desreux, V. *Bull. Soc. Chim. Belge* 1954, **63**, 285
- 7 Nakata, M. *Makromol. Chem.* 1971, **149**, 99
- 8 Outer, P., Carr, C. I. and Zimm, B. H. *J. Chem. Phys.* 1950, **18**, 830
- 9 Rahlwes, D. and Kirste, R. G. *Makromol. Chem.* 1977, **178**, 1793
- 10 Cohn-Ginsberg, E., Fox, T. G. and Masson, H. F. *Polymer* 1962, **3**, 97
- 11 Allen, G., Booth, C., Hurst, S. J., Jones, M. N. and Price, C. *Polymer* 1967, **8**, 391
- 12 Beech, D. R. and Booth, C. *J. Polym. Sci. (A-2)* 1969, **7**, 575
- 13 Inagaki, H., Suzuki, H. and Kurata, M. *US-Japan Seminar in Polymer Physics, Kyoto*, 1965
- 14 Bohdanecky, M. *J. Polym. Sci. (B)* 1965, **3**, 201
- 15 Cowie, J. M. G. *Polymer* 1966, **7**, 487
- 16 Yamamoto, A., Fujii, M., Tanaka, G. and Yamakawa, H. *Polym. J.* 1971, **2**, 799