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H. U. Khan[a]; K. Kumar[a]
[a] Indian Institute of Petroleum, Dehradun, India

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A Modified Method for Estimating Unperturbed Dimensions of Macromolecules from Viscosity Data

H. U. KHAN and K. KUMAR

Indian Institute of Petroleum
Dehradun 248005, India

ABSTRACT

A new empirical equation is presented which modifies the Krigbaum equation for calculating K_θ values from measurements of intrinsic viscosity in good solvents. This is found to fit the molecular weight data better for the polymer systems investigated.

INTRODUCTION

The unperturbed mean-square end-to-end distance of a polymer chain ($\overline{r}_0^2$) can be obtained from its intrinsic viscosity in a theta (θ) solvent, i.e., $[\eta]_\theta$ and the molecular weight ($\overline{M}$) by using the Flory and Fox [1] equation

$$\overline{r}_0^2 = \left[\frac{[\eta]_\theta \overline{M}}{\phi}\right]^{2/3} \tag{1}$$

where ϕ is a universal constant.

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When the viscosity is measured in a nontheta solvent, $[\eta]_\theta$ can be determined by applying

$$[\eta]^{2/3}\overline{M}^{1/3} = K_\theta^{2/3} + K_\theta^{5/3}C_T[\eta]^{-1}\overline{M} \tag{2}$$

where $K_\theta = [\eta]_\theta \overline{M}^{-1/2}$ and C_T is a thermodynamic parameter which is zero for a θ solvent.

Later, to simplify this, Krigbaum [2] suggested the following semiempirical equation relating $[\eta]$ in nontheta solvents to $[\eta]_\theta$.

$$[\eta] = K_\theta\overline{M}^{1/2} + 5 \times 10^{-3}\ A_2\overline{M} \tag{3}$$

where A_2 is a second virial coefficient

Besides these, various other correlations, both empirical and semiempirical, have been put forward from time to time for calculating $\overline{r}_0^2$. For example, those of Kurata and Stockmeyer [3], Stockmeyer and Fireman [4], Cowie [5], and Bohdanecky [6].

All these relationships, because of their empirical nature, have been found to be of limited application [7]. While attempting to apply the Krigbaum equation (Eq. 3) in some of our experimental and literature data, it was found that K_θ values are higher than the published ones in θ solvents, and in some cases $[\eta]/\overline{M}^{1/2}$ values are not exactly linear function of $\overline{M}^{1/2}$. We have made attempts to find a purely empirical relationship from our data and those in the literature data which will be more accurate.

DATA AND DISCUSSION

The applicability of the Krigbaum equation was checked for several systems using data from the published literature. These confirmed deviation from the published K_θ values (Table 1). Therefore we tried to correlate the data through a modified equation which would be generally applicable to all or at least to most of the systems. Literature data on the following six polymer solvent systems, together with their fractionation data, were used to examine this relationship.

1. Polyvinyl acetate (PVAc) in acetone at 25°C [8]
2. Natural rubber in benzene at 30°C [9]
3. Cellulose tricaprylate in toluene at 30°C [10]
4. Cellulose triester in methyl ethyl ketone at 60°C [10]
5. Crystal polystyrene from Aquinto organic France (PS/550) in toluene at 30°C [11]
6. PS/550 in ethyl acetate at 30°C [11]

TABLE 1

Sample	Solution/solvent system	Temperature (°C)	$K_\theta \times 10^4$ literature experimental values	$K_\theta \times 10^4$ Krigbaum equation	$K_\theta \times 10^4$ modified equation
1	PVAc/acetone	25	8.7	12.6	8.8
2	Natural rubber/benzene	30	11.9	17.3	12.6
3	Cellulose tricaprylate/ benzene/toluene	30	12.9 ± 0.4	12.6	12.6
4	Cellulose tributyrate/ MEK	60	8.4 ± 0.2	10.6	7.3
5	PS/550/toluene	30	Not available	8.2	6.5
6	PS/550/ethyl acetate	30	Not available	8.0	8.0

Trial and error calculations based on these data showed that plots of $[\eta]/\overline{M}^{1/2}$ vs $\overline{M}^{0.35}$ give a better linear relationship for all these systems. Consequently, these results can be better represented by

$$[\eta]/\overline{M}^{1/2} = K_\theta + A_2\overline{M}^{0.35} \tag{4}$$

This equation determines K_θ from the extrapolation of $\overline{M}^{0.35}$ to zero, i.e., to small molecular limits. This relationship (Eq. 4), like that of Krigbaum, gives a physically reasonable answer in the sense that as the solvent tends toward θ conditions, the second term on the right-hand side tends toward zero.

Plots of $[\eta]/\overline{M}^{1/2}$ vs $\overline{M}^{1/2}$ and $\overline{M}^{0.35}$ are shown graphically in Figs. 1 and 2. The values of K_θ and A_2 calculated using Eq. (4) for each system under study are given in Table 2. By taking these values of K_θ and substituting the values of $\overline{M}$ in the equation $K_\theta = [\eta]_\theta\overline{M}^{1/2}$,

$[\eta]_\theta = 8.8 \times 10^{-4}\ \overline{M}^{1/2}$ for PVAc in acetone at 25°C

$= 12.6 \times 10^{-4}\ \overline{M}^{1/2}$ for natural rubber in benzene at 30°C

$= 12.6 \times 10^{-4}\ \overline{M}^{1/2}$ for cellulose tricaprylate in toluene at 30°C

$= 7.7 \times 10^{-4}\ \overline{M}^{1/2}$ for cellulose triester (cellulose tributyrate) in methyl ethyl ketone at 60°C

$= 6.5 \times 10^{-4}\ \overline{M}^{1/2}$ for PS/550 in toluene at 30°C

$= 8.0 \times 10^{-4}\ \overline{M}^{1/2}$ for PS/550 in ethyl acetate at 30°C

The values of $\overline{r}_0^2$ can then be found by using these values in Eq. 1.

CONCLUSION

The accuracy of Eq. (4) was checked by calculating the K_θ values for the system under study and comparing them with those from the literature as well as with Eq. (3). These are also given in Table 1. The agreement between the values obtained from Eq. (4) and the literature values appears to be quite satisfactory; it is therefore inferred that Eq. (4) will be applicable to a wide variety of systems.

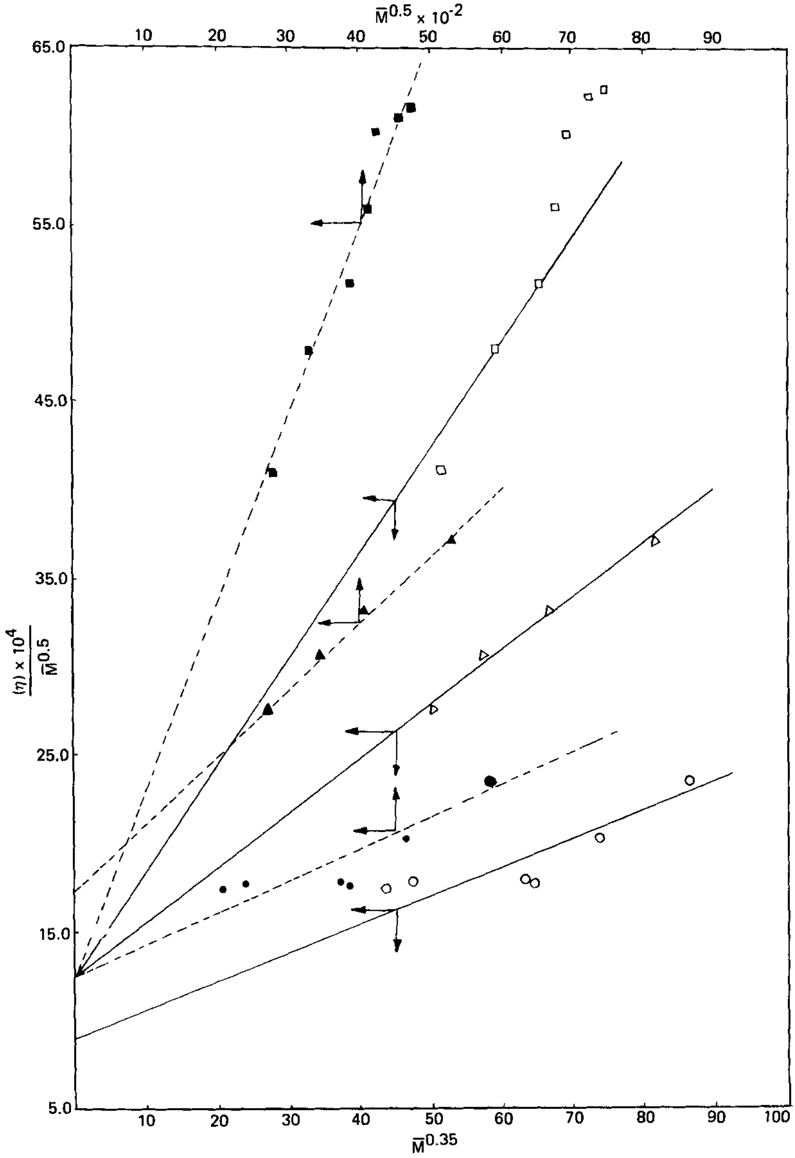

FIG. 1. Plot of $\frac{[\eta] \times 10^4}{\bar{M}^{1/2}}$ vs $\bar{M}^{1/2}$ (- -) and $\frac{[\eta] \times 10^4}{\bar{M}^{1/2}}$ vs $\bar{M}^{0.35}$ (—) employing Eqs. (3) and (4). (○, ●) PVAc-acetone at 25°C, (△, ▲) natural rubber-benzene at 30°C, and (□, ■) cellulose tricaprylate-toluene at 30°C.

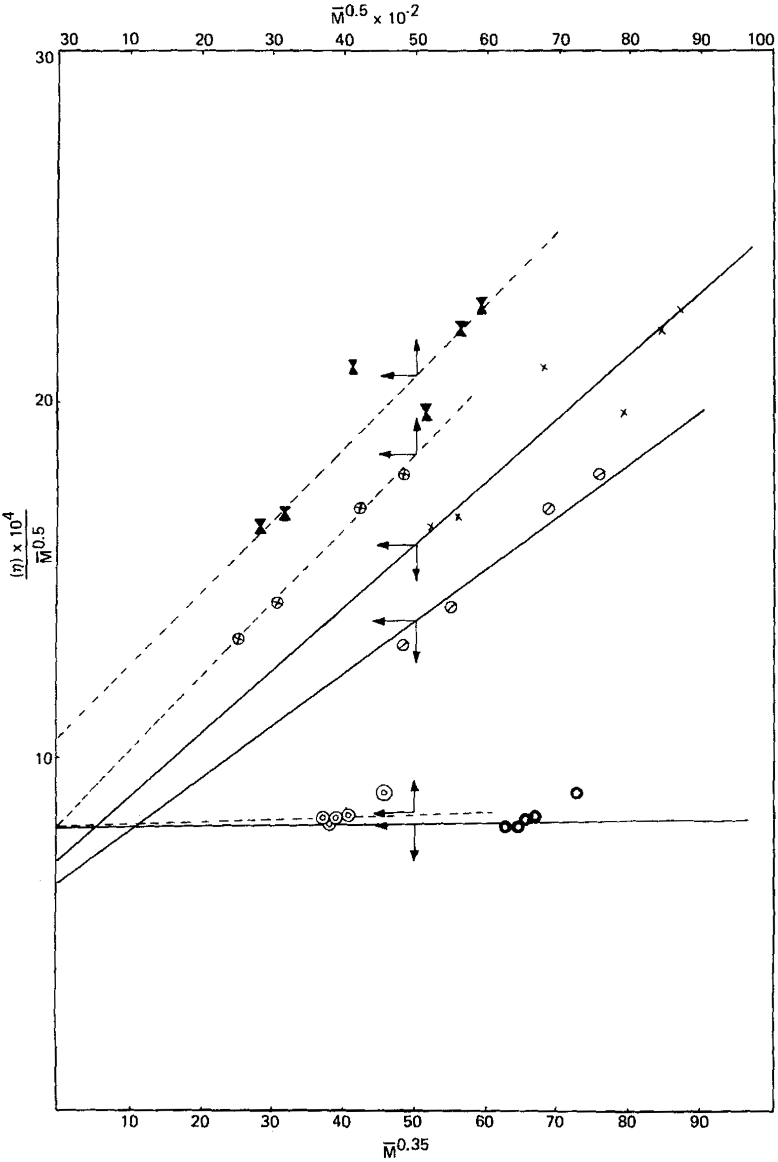

FIG. 2. Plot of $\frac{[\eta] \times 10^4}{\overline{M}^{1/2}}$ vs $\overline{M}^{1/2}$ (- -) and $\frac{[\eta] \times 10^4}{\overline{M}^{1/2}}$ vs $\overline{M}^{0.35}$ (—) employing Eqs. (3) and (4). (o,◎) PS-ethyl acetate at 30°C, (⊕, ⊘) PS-toluene at 30°C, (⧗,×) cellulose triester-MEK at 60°C.

TABLE 2

Sample	Solution/solvent system	Temperature (°C)	$K_\theta \times 10^4$ modified equation	$A_2 \times 10^5$ modified equation
1	PVAc/acetone	25	8.8	1.62
2	Natural rubber/ benzene	30	12.6	3.07
3	Cellulose tricaprylate/ toluene	30	12.6	6.00
4	Cellulose tributyrate/MEK	60	7.3	1.66
5	PS/550/toluene	30	6.5	1.01
6	PS/550/ethyl acetate	30	8.0	0.03

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REFERENCES

[1] P. J. Flory and T. G. Fox, J. Am. Chem. Soc., 73, 1904 (1951).
[2] W. R. Krigbaum, J. Polym. Sci., 18, 315 (1950); Ibid., 28, 213 (1958).
[3] M. Kurata and W. H. Stockmeyer, Fortschr. Hochpolym.-Forsch, 3, 196 (1963).
[4] W. H. Stockmeyer and M. Fixman, J. Polym. Sci., C1, 137 (1963).
[5] J. M. G. Cowie, Polymer, 7, 487 (1966).
[6] M. Bohdanecky, J. Polym. Sci., A3, 201 (1965).
[7] D. C. Blackby, Addition Polymers—Formation and Characterization, Plenum, New York, 1968, pp. 208-211.
[8] W. R. Moore and M. Murphy, J. Polym. Sci., 56, 519 (1962).

[9] H. L. Wagner and P. J. Flory, J. Am. Chem. Soc., 74, 195 (1952).
[10] L. M. Kern and P. J. Flory, Ibid., 74, 2517 (1952).
[11] H. U. Khan and K. V. C. Rao, Indian J. Technol., 15(5), 215 (1977).

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