On the Single-Point Determination of Intrinsic Viscosity

It is convenient to measure the intrinsic viscosity of a polymer solution $[\eta]$ from a single-point determination using equations proposed in the literature.[1,2] However, we have been worried about the accuracy of this procedure as compared with the multipoint method based on Huggins' equation:

$$\eta_{sp} = [\eta]c + K' [\eta]^2c^2 \tag{1}$$

where the specific viscosity, η_{sp}, is the relative viscosity $\eta_r - 1$ at concentration c, and K' is Huggins' constant.

As pointed out by Palit and Kar,[2] various single-point equations can be derived from eq. (1) using the expansion

$$\ln \eta_r = \ln (1 + \eta_{sp}) = \eta_{sp} - {}^1/_2\, \eta_{sp}^2 + {}^1/_3\, \eta_{sp}^3 - {}^1/_4\, \eta_{sp}^4 \tag{2}$$

if K' is assumed to be zero.

By neglecting terms above quadratic in eq. (2), they deduced the equation proposed by Solomon and Ciuta[1]:

$$[\eta] = \frac{1}{c} (2\eta_{sp} - 2 \ln \eta_r)^{1/2}. \tag{3}$$

However if one substitutes $1 + \eta_{sp}$ for η_r in eq. (3), then expansion gives

$$[\eta]\, c = \eta_{sp} (1 - {}^2/_3\, \eta_{sp})^{1/2} \tag{4}$$

and expanding the square root and solving for η_{sp} gives

$$\eta_{sp} = \frac{3 - (9 - 12\, [\eta]\, c)^{1/2}}{2}, \tag{5}$$

which upon expansion of the square root leads to

$$\eta_{sp} = [\eta]\, c + {}^1/_3\, [\eta]^2\, c^2. \tag{6}$$

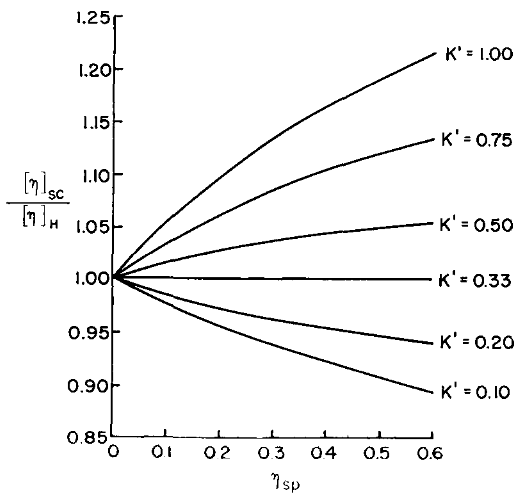

Fig. 1. A comparison of the intrinsic viscosity determined by the single-point method of Solomon and Cuita and the multipoint method using the Huggins equation.

The single-point method using eq. (3) should therefore give results in agreement with Huggins' equation when $K' = {}^1/_3$. For values of $K' > {}^1/_3$, this single-point method gives results for $[\eta]$ denoted by $[\eta]_{sc}$ which are higher than the values obtained by the multipoint method $[\eta]_H$. For $K' < {}^1/_3$, $[\eta]_{sc}$ is less than $[\eta]_H$. The ratio $[\eta]_{sc}/[\eta]_H$ is illustrated in Figure 1 as a function of η_{sp}.

By assuming $K' = 0$ and including the cubic term in eq. (2), Palit and Kar[2] deduced the single-point equation proposed by Deb and Chatterjee.[3] By algebraic expansion as outlined above it can be shown that the Deb and Chatterjee equation should agree with the Huggins equation when $K' = {}^1/_4$. Similarly by including the biquadratic terms in eq. (2), a single-point equation is obtained which agrees with the Huggins equation when $K' = {}^1/_5$. Thus the divergence between the single-point and multipoint methods will become larger as more terms are included in eq. (2) provided $K' > {}^1/_3$; it is not necessarily due to errors in measuring η_{sp} as suggested by Palit and Kar.[2] Clearly, the value of K' must be known in order to select the single-point equation in best agreement with Huggins' equation.

References

1. O. F. Solomon and I. Z. Ciuta, *J. Appl. Polym. Sci.*, **6**, 686 (1962).
2. S. R. Palit and I. Kar, *J. Polym. Sci. A-1*, **5**, 2629 (1967).
3. P. C. Deb and S. R. Chatterjee, unpublished work cited in ref. 2.

T. GILLESPIE
M. A. HULME

Department of Fisheries and Forestry
Forestry Branch
Forest Products Laboratory
Ottawa, Canada

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