On the Single-Point Determination of Intrinsic Viscosity

Many equations[1-4] are available for obtaining the intrinsic viscosity $[\eta]$ by determining the viscosity of a polymer solution at a single concentration C. All these equations are applicable in a certain range of Huggins' constant k and $[\eta]C$.

Recently Berlin[5] proposed a method, similar in principle to that of Maron,[6] of the single-point determination of $[\eta]$, based on the equation of Huggins,

$$\eta_{sp}/C = [\eta] + k[\eta]^2C, \tag{1}$$

and on that of Kraemer,[7]

$$\ln \eta_{rel}/C = [\eta] + (k - 0.5)[\eta]^2C \tag{2}$$

In Berlin's terminology, $A = a = [\eta]$, $B = k[\eta]^2$, and $b = (k - 0.5)$. Although he mentions that the proposed method is limited by the possibility of departure from linearity of eqs. (1) and (2), it is emphasized that it is applicable to any polymer–solvent system with the same degree of accuracy as the extrapolation method and is, therefore, free from the disadvantage of knowing a constant associated with the nature of the polymer solution.

It has already been shown by Shroff,[8] Pechoc,[9] and by Ibrahim[10] that eq. (2) or the one derived by subtraction of eq. (2) from eq. (1) is an insufficient approximation of eq. (1). Furthermore, Ibrahim has shown that the Huggins equation (1) is an insufficient approximation of that of Schulz and Blaschke:[11]

$$\eta_{sp}/C = [\eta] + k[\eta]\eta_{sp} \tag{3}$$

or

$$C/\eta_{sp} = 1/[\eta] - kC \tag{3a}$$

The correct determination of $[\eta]$ and k should thus involve a plot of η_{sp}/C versus η_{sp} or of C/η_{sp} versus C. The use of eq. (1) rather than eq. (2) or (3a) can lead to an error[10] of as much as 30% in $[\eta]$ and 300% in k. An error of 20% in $[\eta]$ can lead to one of 40% in the molecular weight $\bar{M}_v$ if the value of the index a in the Staudinger equation $[\eta] = K\bar{M}_v{}^a$ is 0.5.

It is, therefore, important to realize that Berlin's method is applicable when $k \approx$ 0.3–0.4, as is usually true of flexible polymers in good solvents. Even in this range, however, the difference between the calculated and the extrapolated values of $[\eta]$ may differ as much as ±5% when $[\eta]C$ equals 2. The method fails for polymer–solvent systems where k is significantly out of this range, even if the values of $[\eta]C$ are low. Some examples of such failures have been given by Shroff and by Pechoc.

The method proposed by Berlin is, therefore, as accurate or limited as other single-point methods. This is further borne out by the fact that the value of $[\eta]C$ calculated by Berlin's method is nearly the same as the values obtained from many other equations[1-4] for single-point determination.

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