

5. Charley, R. V., *J. Appl. Polymer Sci.*, **6**, S19 (1962).
6. Charley, R. V., *Brit. Plastics*, **38**, 476 (1961).
7. Skinner, S. J., *J. Appl. Polymer Sci.*, **5**, S5 (1961).
8. Mendelson, R. A., private communication.

RICHARD L. BALLMAN

Monsanto Chemical Company
Plastics Division
Springfield, Massachusetts

Received December 4, 1962

Single Point Determination of Intrinsic Viscosity

In a recent paper, Solomon and Ciută¹ propose an equation for obtaining the intrinsic viscosity of a polymer by the measurement of the viscosity of the polymer in solution at a single concentration. The proposed equation is:

$$[\eta] = 1/C \sqrt{2(\eta_{sp} - \ln \eta_{rel})} \quad (1)$$

These authors arrived at this equation experimentally, and justify its validity on the grounds that $1/C \sqrt{2(\eta_{sp} - \ln \eta_{rel})}$ tends to $[\eta]$ as C tends to zero.

In our laboratories we have been using this same equation, which we derived analytically using Huggins' relation:

$$\frac{\eta_{sp}}{C} = [\eta] + K_1[\eta]^2 C \quad (2)$$

The derivation is as follows:

$$\eta_{sp} = [\eta]C + K_1[\eta]^2 C^2 \quad (3a)$$

$$\eta_{rel} = 1 + [\eta]C + K_1[\eta]^2 C^2 \quad (3b)$$

$$\ln \eta_{rel} = \ln \{1 + [\eta]C + K_1[\eta]^2 C^2\} \quad (3c)$$

Expanding into series, neglecting terms in C^3 and higher, and re-arranging, leads to:

$$\ln \eta_{rel} = [\eta]C + [\eta]^2(K_1 - 1/2)C^2 \quad (4)$$

Subtracting (4) from (3a), one obtains:

$$\eta_{sp} - \ln \eta_{rel} = 1/2[\eta]^2 C^2 \quad (5)$$

Transposing, (5) leads directly to (1).

As Solomon and Ciută point out, eq. (1) is a "universal" relation permitting determination of intrinsic viscosities by a single point measurement, without having to use any constants which depend on the interaction of the polymer-solvent system. It is important to realize, however, that the validity of eq. (1) for any polymer-solvent system depends only on the validity of the Huggins' equation for that system, since eq. (1) is derived therefrom. On the other hand, use of eq. (1) in conjunction with the classical three point determination and graphical extrapolation is sufficient to establish whether the Huggins equation applies for a given polymer-solvent system. If the $[\eta]$ obtained by graphical extrapolation agrees with the $[\eta]$ obtained by use of eq. (1) then the Huggins relation applies. Equation (4) also shows that for values of $K_1 > 1/2$, plots of $1/C \ln \eta_{rel}$ vs. C (used in the determination of inherent viscosities) will have a positive, rather than the usual negative slope.

References

1. Solomon, O. F., and I. Z. Ciutá, *J. Appl. Polymer Sci.*, **6**, 683 (1962).

R. Z. NAAR
H. H. ZABUSKY
R. F. HEITMILLER

Cabot Corporation
Billerica, Massachusetts

Received February 11, 1963