Correct Determination of Intrinsic Viscosity

Introduction

The best known equations for determination of $[\eta]$ are those of Kraemer[1] (1) Huggins[2] (2) and Schulz and Blaschke[3] (3).

$$\ln \eta_{rel}/c = [\eta] + (k - 0.5)[\eta]^2 c \tag{1}$$

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

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

These equations give also the value for k (Huggins' constant)

Discussion

Schultz and Blaschke[3] arrived empirically at eq. (2), while Huggins[2] derived—by an extension of Kuhn's hydrodynamical treatment—the equation:

$$\eta_{sp}/c = [\eta]/(1 - k[\eta]c) \tag{4'}$$

There are two main conditions for applicability of this equation: the first one is the mathematical condition that $k([\eta])c$ must be smaller than one; the second condition is that c must be small enough to prevent an interaction between two molecules of polymer.

On expanding eq. (4) in series, the form will be:

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c + k^2[\eta]^3 c^2 + k^3[\eta]^4 c^3 + \ldots \tag{4}$$

From this equation, neglecting the terms c^n with $n > 2$, Huggins obtained his well-known equation (2).

On the other hand, it can be shown that Kraemer's equation is also an approximation of eq. (4) by using:

$$\ln \eta_{rel} = \ln (1 + \eta_{sp}) = \frac{\eta_{sp}}{1} - \frac{\eta_{sp}^2}{2} + \frac{\eta_{sp}^3}{3} - \frac{\eta_{sp}^4}{4} + \ldots \tag{5}$$

and

$$\frac{\ln \eta_{rel}}{c} = \frac{1}{1}\frac{\eta_{sp}}{c} - \frac{1}{2} c\left(\frac{\eta_{sp}}{c}\right)^2 + \frac{1}{3} c^2\left(\frac{\eta_{sp}}{c}\right)^3 - \frac{1}{4} c^3\left(\frac{\eta_{sp}}{c}\right)^4 + \ldots \tag{6}$$

then by combining eq. (4') with eq. (6) and also neglecting the terms c^n with $n \geq 2$ we obtain Kraemer's equation, eq. (1).

It is obvious that Huggins' approximation is in any case better than Kraemer's.

Ibrahim[4] showed that the form (4) is identical with Schulz and Blaschke's form (3) after a short transformation:

$$\eta_{sp}/c = [\eta]/(1 - k[\eta]c) \tag{4}$$

$$\eta_{sp}/c(1 - k[\eta]c) = [\eta] \tag{4a}$$

$$\eta_{sp}/c - k[\eta]\eta_{sp} = [\eta] \tag{4b}$$

and

$$\eta_{sp}/c = [\eta] + k[\eta]\eta_{sp} \tag{4c}$$

which is identical with eq. (3).

Proposing to plot the parabola resulting from eq. (4') by neglecting the terms c^n with $n > 2$ and showing experimental data, Ibrahim in the same paper[4] came to the conclusion that Huggins' equation, (2) is nothing but an approximation of eq. (3) or eq. (4), considering the theory of Huggins himself.
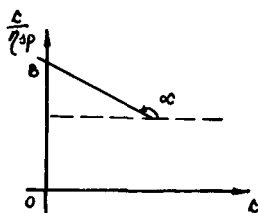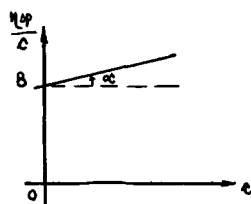
Figure 1.

Figure 2.

Starting from the idea of using the best form (4) for $[\eta]$ determination and at the same time to use the simplest plot we transformed the form (4) as follows. By inverting we got from eq. (4)

$$c/\eta_{sp} = (1 - k[\eta]c)/[\eta] \qquad (7)$$

and continuing we arrived at the form:

$$c/\eta_{sp} = -kc + (1/[\eta]) \qquad (8)$$

Plotting c/η_{sp} against c we get a straight line.

The c/η_{sp} axis intercept gives the reciprocal value of $[\eta]$ and the slope of the line gives the value of k with changed sign.

Instead of plotting η_{sp}/c against c by using the Huggins' form, eq. (2), as is shown in Figure 1 we propose to plot c/η_{sp} against c as is shown in Figure 2 by using eq. (8).

Conclusions

Using the form (8) for determination of $[\eta]$ and also for determination of k we used in the last analysis the equation of Schulz and Blaschke's (3) or Huggins (4).

The form [eq. (8)] which was deduced, permitted the simplest plot as a straight line.

The points which are not on this line represent errors or they are not in the field of sufficient small c to verify the eq. (4).

References

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