Novel Methods for Efficient Estimate of Intrinsic Viscosity

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Synopsis

Two novel procedures have been established to estimate the intrinsic viscosity and the Huggins constant accurately. It is shown that these numerical methods are superior to the existing models, namely the Huggins, Nagy–Kelven–Tudos, and Reilly–Van Der Hoff–Ziogas equations. This finding is attributed to the more even distribution of errors in the dependent variables of the present analyses. The viscometic data of a poly(vinyl chloride) sample in tetrahydrofuran are analyzed by the foregoing five approaches whose accuracies are compared in terms of their variances of estimates.

INTRODUCTION

Dilute-solution viscometry is a simple and reliable tool for characterizing the molecular weights of polymers. This particular method rests on the familiar Mark–Houwink–Sakurada equation which relates the viscosity-average molecular weight M_v to the intrinsic viscosity $[\eta]$. A number of techniques has been developed to assess the $[\eta]$ including various single-point measurements,[1,2] as well as a semiempirical approach.[3] However, $[\eta]$ is conventionally determined by using the Huggins equation[4] derived for nonelectrolyte polymers and given as

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

where η_{sp} is the specific viscosity of the polymer solution of concentration C and k is the Huggins constant. Practically we have

$$\eta_{sp} = t/t_0 - 1 \tag{2}$$

where t_0 and t are the efflux times of the pure solvent and the dilute polymer solution respectively.

Apparently, a plot of η_{sp}/C vs. C according to eq. (1) yields a straight line whose intercept and gradient render the values of $[\eta]$ and k, respectively. Nevertheless, the results thus obtained are highly biased since the variance of the left-hand quantity is not a constant. To the best of our knowledge, two suggestions have been but forward so far to overcome this shortcoming. Nagy, Kelven, and Tudos (NKT)[5] have introduced an improved graphical method, whereas Reilly, Van Der Hoff, and Ziogas (RVZ)[6] have advanced a three-parameter equation for evaluating $[\eta]$. In this work, two new procedures are proposed to enhance the precision of $[\eta]$ estimation.

LEAST-SQUARES METHOD

The least-squares analyses of the Huggins, NKT, and RVZ equations are outlined in the Appendix.

The first novel numerical method is based on a quadratic form of eq. (1), i.e.,

$$\eta_{sp} = [\eta]C + k[\eta]^2 C^2 \tag{3}$$

Hence the variance of the lhs is independent of C which may vary by a few folds:

$$V(\eta_{sp}) = \left(\frac{t_0^2 + t^2}{t_0^4}\right) V(t) \tag{4}$$

Solving eq. (3) by the least-squares technique results in

$$[\eta] = \frac{\Sigma C^4 \Sigma \eta_{sp} C - \Sigma C^3 \Sigma \eta_{sp} C^2}{\Sigma C^2 \Sigma C^4 - (\Sigma C^3)^2} \tag{5}$$

$$k = \frac{1}{[\eta]^2} \frac{\Sigma C^2 \Sigma \eta_{sp} C^2 - \Sigma C^3 \Sigma \eta_{sp} C}{\Sigma C^2 \Sigma C^4 - (\Sigma C^3)^2} \tag{6}$$

It can be shown that their respective variances are

$$V[\eta] = \left[\frac{1}{\Sigma C^2 \Sigma C^4 - (\Sigma C^3)^2}\right]^2 \left[\sum_i (C_i \Sigma C^4 - C_i^2 \Sigma C^3)^2 \left(\frac{t_0^2 + t_i^2}{t_0^4}\right)\right] V(t) \tag{7}$$

$$V(k) = \frac{V(\beta)}{[\eta]^4} + \left(\frac{2k}{[\eta]}\right)^2 V[\eta] - \frac{4k}{[\eta]^3} \text{Cov}([\eta],\beta) \tag{8}$$

where

$$V(\beta) = \left[\frac{1}{\Sigma C^2 \Sigma C^4 - (\Sigma C^6)^2}\right]^2 \left[\sum_i (C_i^2 \Sigma C^2 - C_i \Sigma C^3)^2 \left(\frac{t_0^2 + t_i^2}{t_0^4}\right)\right] V(t) \tag{9}$$

$$\text{Cov}([\eta],\beta) = \left[\frac{1}{\Sigma C^2 \Sigma C^4 - (\Sigma C^3)^2}\right]^2 \left[\sum_i (C_i \Sigma C^4 - \right.$$
$$\left. C_i^2 \Sigma C^3)(C_i^2 \Sigma C^2 - C_i \Sigma C^3)\left(\frac{t_0^2 + t_i^2}{t_0^4}\right)\right] V(t) \tag{10}$$

Recently a dependable algorithm which considers the presence of error in all variables has been successfully applied to evaluate the monomer reactivity ratios in copolymerization.[7] This error-in-variable method (EVM) is now applied to the present study with a minor modification by setting $V(C) = 0$.

We first define the residual of efflux time r as the difference between the observed and estimated efflux times, i.e.,

$$r = t - t_0 - t_0[\eta]C - t_0k[\eta]^2C^2 \tag{11}$$

The sum of the weighted squares of residual S becomes[8]

$$S = \Sigma \, Wr^2 \tag{12}$$

where W is equal to the reciprocal of variance of r, $V(r)$, i.e.,

$$W = 1/V(r) \tag{13}$$

If the first approximations of $[\eta]$ and k designated, respectively, by $[\eta]'$ and k' are predetermined, then eq. (11) can be expressed by a Taylor series truncated after the first power terms of $[\eta]$ and k to achieve

$$S = \Sigma[L[\eta] + Mk + N]^2 \tag{14}$$

where

$$L = -(t_0C + 2t_0k'[\eta]'C^2)\sqrt{W'} \tag{15}$$

$$M = -t_0[\eta]'^2C^2\sqrt{W'} \tag{16}$$

$$N = (t - t_0 + 2t_0k'[\eta]'^2C^2)\sqrt{W'} \tag{17}$$

$$W' = [(2 + [\eta]'^2C^2 + k'^2[\eta]'^4C^2)V(t)]^{-1} \tag{18}$$

According to the principle of least-squares the derivatives of S with respect to $[\eta]$ and k must be zero. Hence it furnishes two normal equations which lead to the second approximations,

$$[\eta]'' = \frac{\Sigma LM\Sigma MN - \Sigma M^2\Sigma LN}{\Sigma L^2\Sigma M^2 - (\Sigma LM)^2} \tag{19}$$

$$k'' = \frac{\Sigma LM\Sigma LN - \Sigma L^2\Sigma MN}{\Sigma L^2\Sigma M^2 - (\Sigma LM)^2} \tag{20}$$

This data manipulation using eqs. (15)–(20) can be iterated by the recursion on $[\eta]$ and k, until they converge to the best estimates $[\eta]^0$ and k^0. It follows that the variances are

$$V[\eta] = \frac{\Sigma M_0^2}{\Sigma L_0^2\Sigma M_0^2 - (\Sigma L_0M_0)^2} \tag{21}$$

$$V(k) = \frac{\Sigma L_0^2}{\Sigma L_0^2\Sigma M_0^2 - (\Sigma L_0M_0)^2} \tag{22}$$

where L_0, M_0, and N_0 are, respectively, equal to the values of L, M, and N computed at $[\eta]^0$ and k^0. In the present investigation, the first approxi-

mations $[\eta]'$ and k' are estimated by the conventional method using eqs. (25) and (26).

RESULTS AND DISCUSSION

Detailed information on the viscometric measurements of a commercial poly(vinyl chloride) (PVC) sample in tetrahydrofuran (THF) at 25°C has been reported by Nagy and co-workers.[5] These data are used for the present purposes.

Table I displays the results produced by the methods discussed in the preceding section for this particular system. The precision of each estimate is indicated by the value of standard deviation, which is the square root of variance.

It is interesting to note that methods 1, 2, and 4 contain three different modes of error structure as represented by eqs. (29), (30), and (4), respectively. Consequently, the estimates of $[\eta]$ and k from the three methods are noticeably different. The quadratic approach which registers the lowest standard deviations of $[\eta]$ and k is therefore the most efficient among them. In fact, the conventional and NKT equations are only marginally different in predicting the values of the two viscometric parameters as shown in Table I. This disapproves the assertion that the latter increases the reliability of parameters considerably.[5]

Although eq. (43) has a uniform error distribution, it does not provide good results as reflected by its high values of standard deviations. In this invariant relationship, the solvent efflux time t_0 is distinctly treated as an additional parameter. This means that its residual sum of squares involved in the least-squares fitting has a degree of freedom less than the other cases. Hence it would affect the precision of predictions and aggravate the estimated variances of t [eq. (31)] in particular. The value of t_0 computed by eq. (46) is equal to 36.894 ss, which agrees remarkably well with the experimental figure of 36.903 ss. However, the estimated standard deviation of efflux time in this particular case is the highest among the five listed methods, indicating that the overall performance of the RVZ model is least satisfactory herein.

TABLE I
Comparison of Precision of Various Methods for
Estimating Intrinsic Viscosity and Huggins Constant

No.	Method	$[\eta]$ (dL/g)	$\sigma([\eta])^a$ (dL/g)	k	$\sigma(k)^b$	$\sigma(t)^c$ (s)
1	Huggins (conventional)	1.001 $(R = 0.9941)^d$	0.018	0.52	0.11	0.026
2	NKT	1.003 $(R = 1.0000)^d$	0.013	0.51	0.11	0.026
3	PVZ	1.013	0.030	0.46	0.15	0.031
4	Quadratic	1.006_1	0.011_2	0.49_3	0.06	0.025
5	EVM	1.006_4	0.010_4	0.49_4	0.06	0.024

[a] Standard deviation of $[\eta]$.
[b] Standard deviation of k.
[c] Standard deviation of t.
[d] Correlation coefficient.

Table I also illustrates that the EVM method offers the best estimates of $[\eta]$ and k as substantiated by the lowest $\sigma(t)$. Evidently, this rigorous analysis improves the results from the Huggins plot significantly. In addition, only two iterations were required to produce these results. If the errors in polymer concentration were indispensable, then eq. (18) should be replaced by

$$W' = [(2 + [\eta]'^2 C^2 + k'^2[\eta]'^4 C^2)V(t) + ([\eta]'^2 + 4k'^2[\eta]'^4 C^2)t_0 V(C)]^{-1} \quad (23)$$

The variances $V(t)$ and $V(C)$ may be determined by repetition of experiments if no prior estimates of them are available.[9] However in most cases the $V(C)$ term is of secondary importance[6] and as such it can be ignored altogether.

Freeman and Manning[10] have cited the Mark–Houwink–Sakurada constants for PVC in THF at 25°C. Using these data, we show that M_v is equal to 8.883×10^4 from the EVM method, which is merely 0.7% higher than that predicted by the Huggins equation. However, this figure of discrepancy would have been much higher if the viscometric data had been collected from a poorer solvent.

As expected, the results from the two novel methods are indeed very close, since the quadratic equation [eq. (3)] has about the same uncertainty in η_{sp} [eq. (4)] for this particular study. This implies that if the relative viscosity (t/t_0) is small, then the simple quadratic procedure may be adequate in this connection. Otherwise, the iterative EVM method must be resorted to for the precise estimations of $[\eta]$ and k.

In conclusion, it has been demonstrated that the reliability and precision of viscometric parameters' estimation are assured by a couple of newly introduced procedures. These novel means may be readily adapted to other physical parameter evaluations such as the number-average molecular weight determination by osmometry and the kinetic rate-constant measurement by dilatometry.[11]

APPENDIX

Since both the Huggins and NKT equations are in the linear forms, they may be generalized by

$$y = a + bx \quad (24)$$

Accordingly, we have made the following substitutions: For the former, $y = (t - t_0)/t_0 C$, $x = C$, $a = [\eta]$, and $b = k[\eta]^2$; for the latter, $y = (t - t_0)/C(\tau - C)t_0$, $x = C/(\tau - C)$, $a = [\eta]/\tau$, and $b = k[\eta]^2 + [\eta]/\tau$, where τ is equal to the sum of the lowest and highest concentrations studied. The linear least-squares analysis of eq. (24) yields

$$a = \frac{(\Sigma x^2)(\Sigma y) - (\Sigma x)(\Sigma xy)}{n(\Sigma x^2) - (\Sigma x)^2} \quad (25)$$

$$b = \frac{n(\Sigma xy) - (\Sigma x)(\Sigma y)}{n(\Sigma x^2) - (\Sigma x)^2} \quad (26)$$

where the summation refers to a set of n data points hereafter. The variances of a and b are computed respectively by

$$V(a) = \sum_i \left(\frac{\partial a}{\partial y_i}\right)^2 V(y_i) \tag{27}$$

$$V(b) = \sum_i \left(\frac{\partial b}{\partial y_i}\right)^2 V(y_i) \tag{28}$$

Here $V(y_i)$ is the variance of y_i, written for the Huggins and NKT equations, respectively, as

$$V(y_i) = \left(\frac{t_0^2 + t_i^2}{t_0^4 C_i^2}\right) V(t) \tag{29}$$

$$V(y_i) = \left[\frac{t_0^2 + t_i^2}{t_0^4(\tau - C_i)^2 C_i^2}\right] V(t) \tag{30}$$

where t_i is the efflux time of polymer concentration C_i. The variance of efflux time t is assumed to be an invariant, i.e., $V(t) = V(t_i) = V(t_0)$. It may be estimated by

$$V(t) = \frac{\sum(t - \hat{t})^2}{n - p} \tag{31}$$

where $\hat{t}$ is the best estimate t and p is the number of unknown parameters. It is noted that p is equal to 2 for all models studied herein except the PVZ method where $p = 3$. However, the variance of C is regarded as vanishingly small, i.e., $V(C) = 0$ in any case. Finally the Huggins equation leads to

$$V[\eta] = V(a) \tag{32}$$

$$V(k) = \frac{V(b)}{a^4} + \left(\frac{2b}{a^3}\right)^2 V(a) - \frac{4b}{a^5} \text{Cov}(a,b) \tag{33}$$

where

$$V(a) = \left[\frac{1}{n \sum C^2 - (\sum C)^2}\right]^2 \left\{\sum_i \left[\frac{\sum C^2 - (\sum C)}{C_i}\right]^2 \left(\frac{t_0^2 + t_i^2}{t_0^4}\right)\right\} V(t) \tag{34}$$

$$V(b) = \left[\frac{1}{n \sum C^2 - (\sum C)^2}\right]^2 \left\{\sum_i \left[\frac{nC_i - (\sum c)}{C_i}\right]^2 \left(\frac{t_0^2 + t_i^2}{t_0^4}\right)\right\} V(t) \tag{35}$$

and the covariance of a and b,

$$\text{Cov}(a,b) = \left[\frac{1}{n \sum C^2 - (\sum C)^2}\right]^2 \left[\sum_i (\sum C^2 - C_i \sum C)(nC_i - \sum C)\left(\frac{t_0^2 + t_i^2}{C_i^2 t_0^4}\right)\right] V(t) \tag{36}$$

Analogously the NKT equation results in

$$V[\eta] = \tau^2 V(a) \tag{37}$$

$$V(k) = \frac{V(b)}{a^4 \tau^4} + \left(\frac{a^2 + 4b^2}{a^6 \tau^4}\right) V(a) + 2\left(\frac{1}{a^4 \tau^4}\right)\left(1 - \frac{2b}{a}\right) \text{Cov}(a,b) \tag{38}$$

where

$$V(a) = \left[\frac{1}{n\Sigma(x')^2 - (\Sigma x')^2}\right]\left\{\sum_i [\Sigma(x')^2 - x'_i(\Sigma x')]^2\left[\frac{t_0^2 + t_0^2}{t_0^4(\tau - C_i)^2 C_i^2}\right]\right\}V(t) \tag{39}$$

$$V(b) = \left[\frac{1}{n\Sigma(x')^2 - (\Sigma x')^2}\right]^2\left\{\sum_i [nx'_i - (\Sigma x')]^2\left[\frac{t_0^2 + t_i^2}{t_0^4(\tau - C_i)^2 C_i^2}\right]\right\}V(t) \tag{40}$$

$$\mathrm{Cov}(a,b) = \left[\frac{1}{n\Sigma x'^2 - (\Sigma x')^2}\right]^2\left\{\sum_i (\Sigma x'^2 - x'_i\Sigma x')(nx' - \Sigma x')\left[\frac{t_0^2 + t_i^2}{t_0^4(\tau - C_i)^2 C_i^2}\right]\right\}V(t) \tag{41}$$

$$x'_i = \frac{C_i}{(\tau - C_i)} \tag{42}$$

The RVZ equation converts eq. (1) to

$$t = t_0 + t_0[\eta]C + t_0 k[\eta]^2 C^2 \tag{43}$$

where t_0 is regarded as a new parameter to be determined. Now the lhs of the equation is of uniform uncertainty. The least-squares solutions of eq. (43) are

$$[\eta] = \frac{A_3 A_4 - A_1 A_6}{A_2 A_6 - A_4 A_5} \tag{44}$$

$$k = \frac{A_4 + A_5 + [\eta]A_7}{[\eta]^2 A_8} \tag{45}$$

$$t_0 = \frac{\Sigma t}{n + [\eta]\Sigma C + k[\eta]^2 \Sigma C^2} \tag{46}$$

where

$$A_1 = n\Sigma tC - \Sigma t\Sigma C \tag{47}$$

$$A_2 = \Sigma tC\Sigma C - \Sigma t\Sigma C^2 \tag{48}$$

$$A_3 = n\Sigma tC^2 - \Sigma t\Sigma C^2 \tag{49}$$

$$A_4 = \Sigma t\Sigma C^3 - \Sigma tC\Sigma C^2 \tag{50}$$

$$A_5 = \Sigma tC^2\Sigma C - \Sigma t\Sigma C^3 \tag{51}$$

$$A_6 = \Sigma t\Sigma C^4 - \Sigma tC^2\Sigma C^2 \tag{52}$$

$$A_7 = \Sigma tC^2\Sigma C^2 - \Sigma tC\Sigma C^3 \tag{53}$$

$$A_8 = \Sigma tC\Sigma C^4 - \Sigma tC^2\Sigma C^3 \tag{54}$$

The variances are calculated by

$$V[\eta] = V(t)\sum_i\left(\frac{\partial[\eta]}{\partial t_i}\right)^2 \tag{55}$$

$$V(k) = V(t)\sum_i\left(\frac{\partial k}{\partial t_i}\right)^2 \tag{56}$$

where the derivatives are obtainable from eqs. (44)–(54).

References

1. O. F. Solomon and B. S. Gotesman, *Makromol. Chem.,* **104,** 177 (1967).
2. H. U. Khan and G. S. Bhargava, *J. Polym. Sci.,* **B18,** 803 (1980).
3. K. K. Chee, *J. Appl. Polym. Sci.,* **23,** 1639 (1979).
4. M. L. Huggins, *J. Am. Chem. Soc.,* **64,** 2716 (1942).
5. T. T. Nagy, T. Kelven, and F. Tudos, *Polymer,* **19,** 1360 (1978).
6. P. M. Reilly, B. M. E. Van Der Hoff, and M. Ziogas, *J. Appl. Polym. Sci.,* **24,** 2087 (1979).
7. K. K. Chee and S. C. Ng, Submitted.
8. W. E. Wentworth, *J. Chem. Educ.,* **42,** 96 (1965).
9. N. R. Draper and H. Smith, *Applied Regression Analysis,* Wiley, New York, 1966.
10. M. Freeman and P. P. Manning, *J. Polym. Sci.,* **A2,** 2017 (1964).
11. S. C. Ng and K. K. Chee, *J. Polym. Sci., Polym. Chem. Ed.,* **20,** 409 (1982).