Statistical Study of the Application of the Huggins Equation to Measure Intrinsic Viscosity

PARK M. REILLY, B. M. E. VAN DER HOFF, and M. ZIOGAS, *University of Waterloo, Waterloo, Ontario, Canada N2L 3Gl*

Synopsis

Intrinsic viscosities of polymers are most often estimated using the Huggins equation, which relates the quotient η_{sp}/c to intrinsic viscosity and concentration c. It is shown that when this method is used, the error structure is distorted by the presence of concentration in the quotient. The result is that when dilution series experiments are analyzed, the estimates are ordinarily poorer the more dilutions are made. A rearrangement of the Huggins equation is introduced which allows precise estimation from any experiment. It is also shown that dilution series experiments with more than three different concentrations including that of the pure solvent are inefficient by any method of analysis, and convenient experiments which may be considered practical optima are described. When they are used the conventional analysis is restored to full efficiency. Design and analysis of experiments where there is important uncertainty in polymer concentration are also studied.

INTRODUCTION

Many physical and technical properties of a polymer of given chemical composition depend strongly on its molecular mass distribution, and it often suffices to characterize this distribution by an average molecular mass. One average mass which is frequently used is the viscosity average in a particular solvent. It is easily obtained from viscosity measurements on dilute solutions by applying the Mark–Houwink–Sakurada equation, which relates the viscosity-average molecular mass to intrinsic viscosity $[\eta]$. Because of this intrinsic viscosity measurements are widely made on a daily basis in industry, thus justifying a study of their efficiency.

In the late thirties it was customary[1] to extrapolate a plot of specific viscosity divided by concentration (η_{sp}/c) versus concentration to find the value of $\lim(\eta_{sp}/c)$, which is the definition[2] of $[\eta]$. This limit is variously referred to as the intrinsic viscosity, the limiting viscosity number, or the Staudinger index.[3] In 1941 Schulz and Blaschke[1] obtained values of $[\eta]$ by extrapolation of η_{sp}/c versus η_{sp} to $\eta_{sp} = 0$, presumably because it was found empirically that their data fitted a straight line better in this type of plot than in the conventional plot.

If η_{sp}/c is linear in η_{sp}, it follows that

$$\eta_{sp}/c = [\eta] + K\eta_{sp} \tag{1}$$

where K is a constant. Later, Huggins[4] derived this equation by hydrodynamic treatment of a model for a randomly kinked polymer chain consisting of a string of submolecules. His derivation involved an empirical factor in Stokes' relation between viscosity and the frictional force per submolecule which arises from its flow through the solution. The equation can be written in series form:

$$\eta_{sp}/c = [\eta]\left(1 + \sum_{n=1}^{\infty} k^n[\eta]^n c^n\right) \tag{2}$$

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The familiar Huggins equation, shown below, results from truncating the summation in eq. (2) after the term linear in c:

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

The constant k_H is called the Huggins constant. Thus, the plot of η_{sp}/c versus c has been given some theoretical underpinning. It is still used in the conventional method of obtaining intrinsic viscosity values. For stiff polymers the Schulz–Blaschke plot is occasionally used.

Many other relations between viscosity of polymer solutions and concentration have been proposed.[5—7] One often still referred to is the empirical relation of Kraemer[7]:

$$(\ln \eta_r)/c = [\eta] + k_K[\eta]^2c \tag{4}$$

where η_r is the relative viscosity and k_K is a constant. When viscosity data are available at only a few concentrations, eqs. (3) and (4) are often used together. Both are linear in c and have the same intercept. This facilitates graphic estimation of $[\eta]$, particularly since k_H is always positive and k_K is nearly always negative.

These equations and other, more complicated relations have been carefully analyzed in the literature. Improved methods of rectilinear extrapolation have been devised to obtain estimates of $[\eta]$ (see the review by Sakai[5] and References 8–13). If accurate values of $[\eta]$ are required, it must be kept in mind that the Huggins relation, even in its nontruncated form, eq. (2), is based on a simple model and contains a number of assumptions. Experiments over a wider range of concentration than usually employed in estimating $[\eta]$ have shown that eqs. (1) and (2) are usually inadequate outside of a limited concentration range. Equation (2) is then replaced by a similar one in which constants k_n are substituted for k^n. If sufficient data are available, it is then possible with the aid of a computer to apply nonlinear regression analysis and thus obtain estimates of $[\eta]$.[13,14] These new estimates can be considered more accurate, not only because more adjustable parameters are used but because they are consistent with theories more detailed than the simple one underlying the Huggins equation.[13,15]

One important factor which to our knowledge has hitherto received no attention is that, when η_{sp} or $\ln \eta_{sp}$ as in eq. (3) or (4) is divided by the concentration, the error in the quotient caused by error in measuring viscosity is magnified at low concentrations. This effect is most pronounced when concentrations are proportional to 1, 1/2, 1/3, 1/4, . . ., as when solutions are made by diluting a single initial one with successive aliquots of solvent.

As the first objective of this paper, we show that when eq. (3) is used in the conventional way to estimate $[\eta]$ from such series with more than two dilutions, the effect is ordinarily so great that expending work in measuring viscosities of more dilute solutions actually results in poorer estimates of $[\eta]$. We also show how eqs. (3) and (4) may be rearranged so that the error structure is improved. We shall see that when the revised equations are used for estimating $[\eta]$, diligence in preparing solutions and measuring their viscosities is rewarded with better estimates of $[\eta]$. We further show how to design experiments so that the estimated intrinsic viscosity obtained by analyzing their results will be as close to the truth as possible. We find an interesting consequence of optimal design to be that eq. (3) may be used directly to analyze the results of optimally designed experiments with no loss in efficiency.

As the final objective of this paper we show the effect of errors in the measurement of concentration and how to deal with them in designing and analyzing experiments.

Equations (3) and (4), the Huggins and Kraemer equations, give nearly the same estimates of $[\eta]$ when the errors are reasonably small. Since however the Kraemer equation is less convenient to use, we confine ourselves to the statistical aspects of the estimation of $[\eta]$ using the Huggins equation. We mainly consider experiments where only a few viscosity measurements are made because of restrictions imposed by the use of commercial Ubbelohde viscometers. It will be assumed that viscosity is proportional to efflux time, that the kinetic energy correction and variations in temperature are negligible, and that there is no adsorption of polymer on the capillary wall.

STATISTICAL ANALYSIS

Apart from the assumptions mentioned above, others have been made and will be discussed at the appropriate times in the following statistical analysis. We assume that errors may be ranked in order of decreasing importance as follows:

1. Errors in measurement of the efflux time of the polymer solution, the largest contributors to which are variations in response time of the observer and variations in temperature.
2. Errors in measurement of the amount of polymer present in the solutions. These result principally from errors in weighing or analysis.
3. Errors in the volume of solution. These arise from variations in the quantity of solvent used in making up the original solution or in diluting it to lower concentrations.

Analysis Neglecting Errors in Concentration

It is instructive and useful to neglect initially the second and third types of errors, which are associated with the concentrations of the polymer solutions, and to focus attention on errors in measurement of efflux time. They may be considered to a good approximation independent and of constant variance.

We start with the Huggins equation in the form

$$\frac{t - \tau}{c\tau} = [\eta] + k_H[\eta]^2 c \tag{5}$$

where t is the efflux time of a solution of concentration c and τ is that of the solvent. This equation is conventionally used to find $[\eta]$ as the y-intercept of a straight line drawn through a plot of the quantity on the left-hand side versus concentration, for a set of data generated from successive dilutions of one original solution.

It is immediately obvious that since τ is constant in any one plot and since the errors in t are assumed to be of constant variance, the variance of the left-hand quantity varies inversely with the square of the concentration. This results in large errors in the ordinates of the points corresponding to low concentrations and consequent errors in the estimate of intrinsic viscosity unless some weighting of the data is used.

One way of avoiding the need for weighting is to rearrange eq. (5) as follows:

$$t = \tau + \frac{\tilde{c}}{d}\tau[\eta] + \frac{\tilde{c}^2}{d^2}\tau k_H[\eta]^2 \tag{6}$$

In recognition of the fact that solutions for viscosity measurements are conveniently prepared by making up one of concentration $\tilde{c}$ and then diluting it with successive aliquots of solvent, we express concentration as $c = \tilde{c}/d$ where $d = 1, 2, \ldots$. The pure solvent may be represented by $d = \infty$.

In Equation 6 the efflux time τ of the pure solvent is regarded as a parameter to be estimated from all the data rather than a quantity measured on the pure solvent alone. Treatment of τ is the same as that of $[\eta]$ and k_H. Since all quantities except d and t are constant Equation 6 represents a parabola when t is plotted against $1/d$. However, the errors in the ordinates of the measured points are now independent and of constant variance. Since in this section we are neglecting the errors in measurement of concentration the standard assumptions of regression analysis[16] apply and for statistical purposes we may write the model as

$$t_i = \tau + \tau[\eta]\frac{\tilde{c}}{d_i} + \tau k_H[\eta]^2\frac{\tilde{c}^2}{d_i^2} + \epsilon_i \qquad i = 1, 2, \ldots, N \tag{7}$$

The subscripts i refer to the ith measurement, including those on the pure solvent. The quantities τ, $[\eta]$ and k_H are parameters to be estimated from the data. The error ϵ_i has been added in accordance with our assumptions.

The fact that there are cross-products among the parameters in Equation 7 dictates that the problem of estimating them be classified as one where the model is nonlinear in the parameters. However, since the least squares estimate of the parameters is unique under these conditions, we may obtain a point estimate of $[\eta]$ as $\hat{\beta}_2/(\hat{\beta}_1\tilde{c})$ with the model rewritten as

$$t_i = \beta_1 + \frac{\beta_2}{d_i} + \frac{\beta_3}{d_i^2} + \epsilon_i \qquad i = 1, 2, \ldots, N \tag{8}$$

The circumflex sign refers to the standard least-squares estimate for models linear in the parameters. While the parabolic relationship between $1/d_i$ and t_i produces some difficulty in graphic estimation of $[\eta]$, the numerical calculation of this proposed estimate is very easy by hand calculator.

An equivalent but more cumbersome way of obtaining the same estimate of $[\eta]$ is by nonlinear parameter estimation using eq. (7) as the model.[16,17] This method does however lead to a good estimate of the variance of the least-squares estimate of $[\eta]$. This is the 2,2 element of $(\mathbf{X}'\mathbf{X})^{-1}\sigma^2$, where σ^2 is the variance of a single measurement of efflux time, $\mathbf{X}$ is the $N \times 3$ matrix the i,j element of which is

$$\left[\frac{\partial f(d_i,\boldsymbol{\theta})}{\partial \theta_j}\right]_{\boldsymbol{\theta} = \hat{\boldsymbol{\theta}}} \tag{9}$$

and $\boldsymbol{\theta}$ is the 3×1 vector the elements of which are τ, $[\eta]$, and k_H. $\hat{\boldsymbol{\theta}}$ is the least-squares estimate of $\boldsymbol{\theta}$. From eq. 7,

$$f(d_i, \boldsymbol{\theta}) = \tau + \tau[\eta]\frac{\tilde{c}}{d_i} + \tau k_H[\eta]^2\frac{\tilde{c}^2}{d_i^2} \tag{10}$$

It is important to recognize that this calculation makes use of the approximation of expanding f in a Taylor series in the elements of θ and truncating it after the first degree terms.

The conventional approach is equivalent to using the model

$$\frac{(t_i - t_0)d_i}{\tilde{c}t_0} = \alpha_1 + \alpha_2 \frac{\tilde{c}}{d_i} + \epsilon_i \qquad i = 1, 2, \ldots, N \tag{11}$$

and estimating α_1 by linear least squares. This is taken as the least-squares estimate of $[\eta]$. The subscript i in this case does not include the measurements of efflux time of the pure solvent. The symbol t_0 represents the average of whatever efflux time measurements are made on the pure solvent.

The estimate of $[\eta]$ obtained in this manner is

$$[\hat{\eta}] = \frac{\sum \frac{1}{d_i^2} \sum t_i d_i - \sum \frac{1}{d_i} \sum t_i}{\tilde{c}t_0 \left[N \sum \frac{1}{d_i^2} - \left(\sum \frac{1}{d_i} \right)^2 \right]} + \frac{N \sum \frac{1}{d_i} - \sum d_i \sum \frac{1}{d_i^2}}{\tilde{c} \left[N \sum \frac{1}{d_i^2} - \left(\sum \frac{1}{d_i} \right)^2 \right]} \tag{12}$$

where each summation sign represents summation over all observations on solutions.

In calculating the variance of this estimate, it must be recognized that there is error in t_0 as well as in each of the t_i. This can be allowed for to a good approximation by the use of the formula for the propagation of variance[18]:

$$\mathrm{Var}[g(\mathbf{u})] = \sum_{i=1}^{n} \left[\frac{\partial g(\mathbf{u})}{\partial u_i} \right]^2_{\mathbf{u} = \tilde{\mathbf{u}}} \mathrm{Var}\, u_i \tag{13}$$

where $g(\mathbf{u})$ is a scalar function of the $n \times 1$ vector random variable $\mathbf{u}$, the elements of which are mutually independent with variances $\mathrm{Var}\, u_i$, $i = 1, 2, \ldots, n$. The vector $\tilde{\mathbf{u}}$ is a set of standard values for the elements of $\mathbf{u}$, often the expectations.

Comparison of Conventional and Proposed Methods of Analyzing Experiments

One favorable property of both methods of estimating $[\eta]$ is that, at least to a good approximation, they are unbiased. As more and more measurements of viscosity are made, the estimates obtained by both methods converge toward the true value. The comparison of the methods then involves only their precision, i.e., reproducibility, as measured by the variances of the estimates.

Table I shows the results of applying both methods to analyze dilution series experiments for various (true) values of the dimensionless quantity $\tilde{c}[\eta]$ which is designated x. An N-trial dilution series experiment is defined as one in which a single solution is made up at concentration $\tilde{c}$ and a single measurement of efflux time (trial) is made at each of dilutions $d = 1, 2, \ldots, N-1$ and on the pure solvent $d = \infty$.

The entries in Table I are the variance factor V and the percent efficiency E, defined by the following equations:

$$\mathrm{Var}\,[\hat{\eta}] = \frac{\sigma^2}{\tau^2 \tilde{c}^2} V \tag{14}$$

$$E = \frac{3V_3}{NV} \times 100 \tag{15}$$

TABLE I
Variance Factor V and Percent Efficiency E for Dilution Series Experiments

Three-trial expts. prop. and conv.			Four-Trial experiments				Five-Trial experiments				Six-Trial experiments			
			V		E		V		E		V		E	
X	V	E	Prop.	Conv.	Prop.	Conv.	Prop.	Conv.	Prop.	Conv.	Prop.	Conv.	Prop.	Conv.
0	26.00	100	21.14	25.28	92.2	77.1	20.73	29.28	75.3	53.3	20.72	34.92	62.7	37.2
0.2	27.24	100	22.52	26.80	90.7	76.2	22.17	31.06	73.7	52.6	22.15	36.97	61.5	36.8
0.4	28.56	100	23.98	28.39	89.3	75.4	23.68	32.92	72.4	52.1	23.65	39.09	60.4	36.5
0.6	29.96	100	25.52	30.07	88.0	74.7	25.27	34.87	71.1	51.6	25.21	41.29	59.4	36.3
0.8	31.44	100	27.14	31.83	86.9	74.1	26.93	36.89	70.0	51.1	26.84	43.58	58.6	36.1
1.0	33.00	100	28.83	33.67	85.8	73.5	28.67	38.99	69.1	50.8	28.54	45.94	57.8	35.9
1.2	34.64	100	30.61	35.58	84.9	73.0	30.48	41.18	68.2	50.5	30.31	48.38	57.1	35.8
1.4	36.36	100	32.46	37.58	84.0	72.6	32.36	43.44	67.4	50.2	32.14	50.90	56.6	35.7
1.6	38.16	100	34.38	39.66	83.2	72.2	34.32	45.79	66.7	50.0	34.04	53.51	56.1	35.7
1.8	40.04	100	36.39	41.81	82.5	71.8	36.34	48.21	66.1	49.8	36.00	56.19	55.6	35.6
2.0	42.00	100	38.47	44.05	81.9	71.5	38.45	50.71	65.5	49.7	38.04	58.95	55.2	35.6

where V is a dimensionless measure of the effect of the design and statistical analysis of the experiment on the variance of the estimate of $[\eta]$. The physical conditions of the experiment, such as viscosity of the solvent, maximum concentration of the solution, etc., only affect the quantities τ, $\bar{c}$, and σ.

In eq. (15), V_3 is V for a three-trial dilution series experiment ($d = 1, 2, \infty$) at the same value of x, N is the number of trials, and E is a measure of the efficiency per trial of the statistical design and analysis of the experiment. It is numerically equal to the number of total trials in a set of repeated 3-trial dilution series experiments needed to produce the same variance of $[\hat{\eta}]$ as 100 repetitions of the experiment being considered would produce.

Several observations may be made on Table I. The first is that the value of k_H does not affect the comparisons. In all cases k_H cancels out of the equations. As might be expected, the proposed analysis gives results always better, and often considerably better, than the conventional analysis, except in the case of three-trial experiments where the results are equal. The reason for the equality is that with three-trial experiments both analyses are fitting a model with three parameters to three experimental points. The difference between the analyses has the effect of only a difference in weighting of the observations: with three points the fit is perfect in both analyses.

A startling consequence of the effect of the improper weighting in the conventional analysis is that, except for four-trial experiments at very low x, the more trials made, the poorer the result as judged by V. With the proposed analysis, V decreases as the number of trials increases, indicating better estimation.

It is also notable that even with the proposed analysis the efficiency per trial decreases sharply as the number of trials in a dilution series experiment increases. It will be seen later that with optimally designed experiments the opposite is true. Consequently, dilution series experiments with more than three trials are always inefficient.

DESIGN OF EXPERIMENTS NEGLECTING ERRORS IN CONCENTRATION

It is relatively easy to establish the highest concentration $\bar{c}$ to use. For $d = 1$, eq. (6) may be written in the form

$$R = 1 + x + k_H x^2 \tag{16}$$

where R is the ratio of the maximum efflux time to the efflux time for pure solvent. This quantity is usually recommended[19] to be not greater than 2, though occasionally higher values are used. If R is chosen to be too high, there is danger that the basic mathematical model, eq. (3), will not apply closely enough; if too low, the experiment will lack precision.

The Huggins constant k_H for many polymer–solvent systems can be found in the literature.[20] Having obtained k_H and chosen R, x may be found by solving eq. (16) and choosing the positive root. The resulting x will rarely exceed 2.

Sometimes an initial estimate of $[\eta]$ will be at hand. If not, an approximation may be obtained by various methods.[9,10,21] The value of $\bar{c}$ may then be obtained by dividing x by $[\eta]$.

An equally important consideration in designing experiments to estimate $[\eta]$ is the precision of the estimate, measured by its variance. In order to establish

this, we first define an experiment as consisting of all the trials which on statistical analysis lead to one estimate of $[\eta]$.

Probably the most popular criterion[22] for the optimal design of experiments for models nonlinear in the parameters is $|\mathbf{X}'\mathbf{X}|$. Under conditions that are usually reasonably realistic, it is approximately inversely proportional to the square root of the (hyper)volume of any particular joint confidence region in parameter space. Hence, an experiment which maximizes $|\mathbf{X}'\mathbf{X}|$ is optimal in the sense that it minimizes the volumes of the joint confidence regions.

In the problem considered here, however, we have no direct interest in τ and k_H, and consequently a better way of optimizing our experiments is simply to choose that one which minimizes the variance of the estimate of $[\eta]$. Strictly, we might prefer to minimize the mean squared error of this estimate, but, since both the conventional and revised methods of analysis are at least approximately unbiased, minimizing the variance is approximately equivalent to minimizing the mean squared error. As stated above, the variance of the estimate of $[\eta]$ using the revised analysis is approximately proportional to the 2,2 element of $(\mathbf{X}'\mathbf{X})^{-1}$. We have chosen this quantity as the criterion for selecting optimal experiments. While it gives results which are somewhat different from those of the $|\mathbf{X}'\mathbf{X}|$ criterion, it is conceptually simpler. Its use however is slightly more complicated.

To produce a general formula for our criterion is cumbersome, but its numerical value is easily calculated from its definition in eq. (9). For comparison purposes, V as defined in eq. (14) is used in order to eliminate the effect of the physical characteristics of the experiment.

THREE-TRIAL EXPERIMENTS

Because the three parameters τ, k_H, and $[\eta]$ must always be estimated, even if only $[\eta]$ is of direct interest, every experiment must consist of at least one trial at each of at least three different concentrations. A simple special case is that where one viscosity measurement is made at concentration $\bar{c}$, corresponding to $d = 1$, and one on the pure solvent, corresponding to $d = \infty$. In this case it is easy to derive an expression for V as a function of x and d, the dilution used at the third trial. When this expression is differentiated with respect to d and equated to zero, the following relation between x and the optimal third dilution $\hat{d}$ is obtained. It is easily verified that $\hat{d}$ does indeed produce a minimum in V:

$$x = 2(1 - \hat{d} + 2\hat{d}^3 - \hat{d}^4)/(\hat{d} - 1)^3 \tag{17}$$

Table II shows V and E for the optimal three-trial experiments for various values of x, the optimal values $\hat{d}$ having been obtained by using eq. (17). As previously, each E in Table II shows the efficiency of the experiment being considered relative to the $d = 1, 2, \infty$ experiment with the same value of x.

It is evident that the $d = 1, \hat{d}, \infty$ experiments are always better than the $d = 1, 2, \infty$ experiments at the same value of x, but by very little. However, the latter are much more convenient in practice because of their integer dilutions. The $1, 2, \infty$ experiments may be considered the practical optima among three-trial experiments.

With four- five-, and six-trial experiments, the situation is similar: the truly optimal experiments do not have integer dilutions, but there always exist ex-

TABLE II

Variance Factor V and Percent Efficiency E for Optimal Experiments

	Optimal Three-trial expts.			Four-Trial experiments				Five-Trial experiments				Six-Trial experiments				N-Trial experiments				
x	$\hat{d}$	V	E	N_1	N_2	N_∞	V	E	N_1	N_2	N_∞	V	E	N_1	N_2	N_∞	V	E	N_1/N	N_2/N	N_∞/N	VN	E
0	1.87	25.71	101.1	1	2	1	18.00	108.3	1	2	2	13.50	115.6	1	3	2	10.83	120.0	0.12	0.50	0.38	64.00	121.9
0.2	1.86	26.90	101.2	1	2	1	19.24	106.2	1	2	2	14.12	115.8	1	3	2	11.45	118.9	0.12	0.49	0.39	67.24	121.5
0.4	1.85	28.16	101.4	1	2	1	20.56	104.2	1	2	2	14.78	115.9	1	3	2	12.11	117.9	0.12	0.48	0.40	70.56	121.4
0.6	1.84	29.50	101.6	1	2	1	21.96	102.3	1	2	2	15.48	116.1	1	3	2	12.81	116.9	0.12	0.47	0.42	73.96	121.5
0.8	1.83	30.91	101.7	1	2	1	23.44	100.6	1	2	2	16.22	116.3	1	3	2	13.55	116.0	0.11	0.45	0.43	77.44	121.8
1.0	1.82	32.40	101.9	1	2	1	25.00	99.0	1	2	2	17.00	116.5	1	3	2	14.33	115.1	0.11	0.44	0.44	81.00	122.2
1.2	1.81	33.96	102.0	1	1	2	25.82	100.6	1	2	2	17.82	116.6	1	2	3	14.88	116.4	0.11	0.43	0.46	84.64	122.8
1.4	1.80	35.60	102.1	1	1	2	26.68	102.2	1	2	2	18.68	116.8	1	2	3	15.45	117.6	0.11	0.43	0.47	88.36	123.4
1.6	1.79	37.32	102.2	1	1	2	27.58	103.8	1	2	2	19.58	116.9	1	2	3	16.05	118.9	0.10	0.42	0.48	92.16	124.2
1.8	1.79	39.12	102.4	1	1	2	28.52	105.3	1	2	2	20.52	117.1	1	2	3	16.68	120.0	0.10	0.41	0.49	96.04	125.1
2.0	1.78	40.99	102.5	1	1	2	29.50	106.8	1	2	2	21.50	117.2	1	2	3	17.33	121.2	0.10	0.40	0.50	100.00	126.0

periments with dilutions of 1, 2, and ∞ which are nearly as good. The practical optima and their V and E values are also shown in Table II. The symbol N_j indicates the number of trials at dilution $d = j$. Note that for experiments with more than three trials the best practical experiment depends to some extent on the value of x.

An interesting and important property of all these best practical experiments is that they provide the same point estimate for $[\eta]$ whether they are analyzed by the conventional or the revised method. This is the consequence of the fact that in each case three parameters are being fitted by data observed at only three concentrations. The common estimate is given in every case by

$$[\hat{\eta}] = \frac{-\bar{t}_1 + 4\bar{t}_2 - 3\bar{t}_\infty}{\tilde{c}\bar{t}_\infty} \tag{18}$$

where $\bar{t}_j$ is the arithmetic average of all of the efflux times measured at dilution $d = j$. The variance of this estimate is given by eq. (14) with

$$V = \frac{1}{N_1} + \frac{16}{N_2} + \frac{(3 + x)^2}{N_\infty} \tag{19}$$

Equation (19) was developed by the use of eq. (13).

The values of E in Table II show that, for an experiment which is optimal for its number of trials, the effectiveness per trial is greater the larger the number of trials. This holds in fact for any number of trials.

If the restriction that N_1, N_2, and N_∞ must be integers is relaxed and if V from eq. (19) is minimized with respect to N_1, N_2, and N_∞ subject to the constraint that their sum is a constant N, it is found that N_1, N_2, and N_∞ must be in proportion to 1, 4, and $3 + x$. Substituting these numbers into eq. (19) gives

$$V = (8 + x)^2/N \tag{20}$$

Of course, it is impossible in practice for the number of trials to have other than integer values. However, the situation described in the last paragraph is approached as N becomes large. Thus, V in eq. (20) may be regarded as the limiting value for an indefinitely large number of trials. This limit of V and the corresponding value of E are shown in the columns for N-trial experiments in Table II for each value of x listed. The optimal number of trials at dilution j is found by multiplying the optimal proportion N_j/N from Table II by N and rounding to the nearest integer.

It is notable that the experiments which are practical optima for $n = 3, 4, 5$, and 6 as shown in Table II are those where N_1, N_2, *and* N_∞ have integer values as close as possible to the proportions 1, 4, and $3 + x$. Since these proportions cannot be reached exactly, V is greater than that given by eq. (20).

Under the assumption of negligible errors in concentration, it will be of no value to make more than one original solution: the desired number of measurements is made by repetition at each dilution, including $d = \infty$. Since ordinarily it requires much less effort to make a measurement of efflux time than to make up a new solution, the recommended experiments will be efficient with respect to effort expended.

If it is desired to make more than a total of six trials, they should be distributed as closely as possible in the optimal proportions. The exact value of V can be calculated for any experiment which involves only dilutions of 1, 2, and ∞ by the use of eq. (19).

DESIGN AND ANALYSIS WHEN THERE ARE ERRORS IN CONCENTRATION

It may happen under some conditions that there will be errors in the measurement of the concentrations of the solutions with sufficient magnitude that they will have a perceptible effect on the estimates of $[\eta]$. We make the assumption that all errors in concentration are caused by imperfect knowledge of the amount of solute present in the solutions; i.e., we assume dilution errors to be negligible.

It can be shown first that eq. (18) still provides an efficient point estimate of $[\eta]$ based on data obtained at $d = 1$, 2, and ∞. Secondly, using eq. (13), the variance of this estimate is found to be given by eq. (14) where now

$$V = \frac{1}{rn_1} + \frac{16}{rn_2} + \frac{(3+x)^2}{N_\infty} + \frac{q^2x^2}{r} \tag{21}$$

This is an extension of eq. (19) to allow for r make-ups of solution of concentration $\tilde{c}$. The efflux time of each of these is measured n_1 times: they are then each diluted with one aliquot of solvent, and the efflux time for each diluted solution is measured n_2 times. As before, there are N_∞ efflux time measurements on the pure solvent. The quantity q is the ratio of the coefficient of variation of the measurement of concentration of the made-up solution to that of the measurement of efflux time of the pure solvent; i.e.,

$$q = \frac{(S.D.\tilde{c})/\tilde{c}}{\sigma/\tau} \tag{22}$$

If we minimize the right-hand side of eq. (21) under the condition that the total number of trials is constant, we find that the number of measurements at each dilution, rn_1, rn_2, and N_∞, should be as close as possible to the proportions 1, 4, and $3 + x$. This is the same result as when there is no error in the measurement of $\tilde{c}$.

As before, the truly optimal experiments require trials at dilutions $d = 1, \hat{d}$, and ∞, where $\hat{d}$ is a noninteger close to 2. The loss of efficiency in using $d = 1$, 2, and ∞, however, is always very small.

The required number of make-ups of solution can always be found by minimizing V in eq. (21) with respect to r. For example, the most important practical decision involves six-trial experiments. Application of eq. (21) shows that if x is less than 1, the optimal experiment is that shown in Table II, $d = 1, 2, 2, 2, \infty, \infty$, with only one make-up of solution for q^2 less than $13/(3x^2)$, and $d = 1, 2, \infty$ for each of two make-ups of solution for greater q^2. If x is between 1 and 2, the optimal experiment is $d = 1, 2, 2, \infty, \infty, \infty$, with only one make-up of solution for q^2 less than $(x^2 + 6x + 6)/(3x^2)$, and $d = 1, 2, \infty$ for each of two make-ups if q^2 is greater.

It is interesting that if r and the numbers of trials are allowed to be continuous variables, there is no optimal r to minimize V with the total number of trials held constant. This situation is approached when the number of trials is large. In that case, the larger the value of r, the better. A minimum in V does occur as described when r and the number of trials are restricted to small integer values.

If however a penalty is placed on make-up of solutions, a minimum value of

V exists under all conditions. More exactly, if r, n_1, n_2, and N_∞ are chosen so as to minimize V under the condition that

$$W = rn_1 + rn_2 + N_\infty + kr \tag{23}$$

is held constant, a minimum in V occurs where rn_1, rn_2, and N_∞ are in the proportions 1, 4, and $3 + x$ as previously, but where

$$r = qxN/(8 + x)k^{1/2} \tag{24}$$

In eqs. (23) and (24), r, n_1, n_2, and N_∞ are considered to be continuous variables, and it requires k times as much effort to make up a new solution as it does to measure a single efflux time. If the numbers of trials are constrained to be small integers, the optimal values of rn_1, rn_2, and N_∞ will be integers with values close to the given proportions and with r close to that given by eq. (24).

Summary of Procedure

1. The maximum concentration $\tilde{c}$ is chosen by the use of eq. (16). Ordinarily, R will have the value 2, and k_H, the Huggins constant, may be found from the literature. The equation is solved for x, which, when divided by a guessed or predetermined value for the intrinsic viscosity, yields the design value for $\tilde{c}$.

2. All experiments which may be considered practical optima involve measurements of efflux time of solutions having dilutions only of 1, 2, and ∞, i.e., concentrations of $\tilde{c}$, $\tilde{c}/2$, and 0.

3. If the error in concentration is small, the number of efflux times to measure at each dilution is read from Table II. The total number of trials and consequently N_1, N_2, and N_∞, are chosen according to the value of x and the desired V. For this, V is obtained by substituting the values of σ, $\tilde{c}$, and τ expected in the measurement along with the desired variance of the estimate of $[\eta]$ into eq. (14).

4. The estimated value of the intrinsic viscosity is obtained by substituting the experimental results into eq. (18).

5. If the error in concentration of solutions is large, the optimal experiment is found by minimizing V in eq. (21). In many practical cases the choice of optimal experiment will be between (a) that shown in Table II for six-trial experiments with only one make-up of solutions and (b) repetitions of the three-trial experiment on each of two make-ups of solution. The criterion for choosing between these is described in the text. After the experiment is performed, the intrinsic viscosity is estimated by using eq. (18) as previously described.

Notation

Latin Letters

c	concentration
$\tilde{c}$	maximum concentration of solution in a set of measurements
d	number of aliquots of solvent added to original solution
$\hat{d}$	optimal dilution
E	efficiency, defined by eq. (15)
f	a mathematical function in eq. (10)

g	a mathematical function in eq. (13)
i	a numbering index, subscript
K	a constant in eq. (1)
k	a constant; in eqs. (23) and (24), the cost of solution make-up
k_H	the Huggins constant, eq. (3)
k_K	a constant in eq. (4)
N	the total number of trials
N_j	the number of trials at dilution j
n_j	the number of trials at dilution j for each make-up of solution
q	a measure of error in concentration, defined by eq. (22)
R	efflux time ratio, eq. (16)
r	number of make-ups of solution in an experiment
s.d.	standard deviation
t	efflux time
t_0	measured efflux time on solvent, eq. (11)
$\bar{t}_j$	average of all efflux times measured at dilution j
$\mathbf{u}$	a vector of random variables
V	variance factor, defined by eq. (14)
V_3	variance factor for a three-trial experiment with $d = 1, 2, \infty$
W	the cost of experimentation; see eq. (23)
$\mathbf{X}$	matrix defined by eq. (9)
$\lvert\mathbf{X}'\mathbf{X}\rvert$	determinant of the matrix product of the transpose of $\mathbf{X}$ by $\mathbf{X}$
x	$\bar{c}[\eta]$, dimensionless intrinsic viscosity

Greek Letters

α_j	parameters in eq. (11), $j = 1, 2, 3$
β_j	parameters in Equation 8, j = 1, 2, 3
ϵ	error in measurement of efflux time
η_r	relative viscosity
η_{sp}	specific viscosity
$[\eta]$	intrinsic viscosity
$\boldsymbol{\theta}$	parameter vector; see eq. (9)
$\hat{\boldsymbol{\theta}}$	least-squares estimate of $\boldsymbol{\theta}$
σ	standard deviation of a measurement of efflux time
τ	true value of efflux time of solvent

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References

1. G. V. Schulz and F. Blaschke, *J. Prakt. Chem. N. F.*, **158,** 130 (1941).
2. E. O. Kraemer and J. Lansing, *J. Phys. Chem.*, **19,** 153 (1935).
3. R. Signer, *Makromol. Chem.*, **17,** 39 (1955–6).
4. M. L. Huggins, *J. Am. Chem. Soc.*, **64,** 2716 (1942).
5. T. Sakai, *J. Polym. Sci., Part A2,* **6,** 1659 (1968).
6. M. Bohdanecky, *Coll. Czech. Chem. Comm.*, **35,** 1972 (1970).
7. E. O. Kraemer, *Ind. Eng. Chem.*, **30,** 1200 (1938).
8. W. Heller, *J. Coll. Sci.*, **9,** 547 (1954).
9. O. F. Solomon and I. Z. Ciuta, *J. Appl. Polym. Sci.*, **6,** 683 (1962).
10. V. Pechoc, *J. Appl. Polym. Sci.*, **8,** 1281, (1964).
11. S. R. Palit and I. Kar, *J. Polym. Sci., Part A1,* **5,** 2629 (1967).
12. P. C. Deb and S. R. Chatterjee, *Makromol. Chem.*, **125,** 283 (1969).
13. A. Rudin, G. B. Strathdee, and W. B. Edey, *J. Appl. Polym. Sci.*, **17,** 3085 (1973).
14. S. H. Maron and R. B. Reznik, *J. Polym. Sci., Part A2,* **7,** 309 (1969).
15. F. W. Ibrahim, *J. Polym. Sci., Part A,* **3,** 469 (1965).
16. N. R. Draper and H. Smith, *Applied Regression Analysis,* Wiley, New York, 1966.
17. Y. Bard, *Nonlinear Parameter Estimation,* Academic Press, New York, 1974.

18. W. Volk, *Applied Statistics For Engineers,* 2nd ed., McGraw-Hill, New York, 1969, p. 155.
19. P. J. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, 1953.
20. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook,* 2nd ed., Wiley, New York, 1975.
21. A. Rudin and R. A. Wagner, *J. Appl. Polym. Sci.,* **19,** 3361 (1975).
22. P. M. Reilly and G. E. Blau, *Can. J. Chem. Eng.,* **52,** 289 (1974).

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