Practical Estimation of Dilute Solution Parameters

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Synopsis

The concentration dependence of viscosities of dilute solutions of nonpolar polymers can be expressed generally as power series in concentration. Intrinsic viscosity is often estimated from zero concentration extrapolations of the Huggins and Kraemer equations, which are truncated versions of virial expressions in concentration. Neither form is strictly valid at most practical concentrations since real curvilinear relationships are forced into rectilinear forms. Prior methods of overcoming this deficiency by basing extrapolation methods for [η] on more extended power series have attempted to provide graphically useful solutions. This requires reduction of the power series to a two-parameter (slope and intercept) form and the assumption of certain relations between the various factors in the initial multiparameter expression. In this work, power series expressions in concentration are solved directly by nonlinear regression analysis. It is shown that no two-parameter solution is generally valid, although each may be of value in a particular context. Three-parameter power series extensions of the basic Huggins and Kraemer equations represent dilute solution viscosities up to concentrations of 1% or 2% (w/v) very well. The computer-assisted nonlinear regression analysis is easily extended to higher powers of concentration, and the use of four-parameter forms is illustrated to represent viscosities of polystyrene solutions with concentrations as high as 9%.

INTRODUCTION

Consideration of the behavior of colloidal suspensions suggests that the concentration dependence of the viscosities of dilute solutions of nonpolar polymers may be expressed generally as a concentration power series.[1] Equation (1) is an example in terms of the specific viscosity η_{sp}:

$$\frac{\eta_{sp}}{c} = [\eta][1 + k_1[\eta]c + k_2[\eta]^2c^2 + k_3[\eta]^3c^3 + \ldots] \tag{1}$$

where $\eta_{sp} = (\eta - \eta_0)/\eta_0$, with η_0 and η being, respectively, the solvent viscosity and the viscosity of a solution of weight concentration c. The limiting viscosity number (intrinsic viscosity) $[\eta]$ is defined as usual as the limiting extrapolated value of η_{sp}/c at zero c.

Practically, $[\eta]$ is conveniently evaluated from experimental η, η_0, and c data by use of graphic representations of the equations of Huggins[2]:

$$\frac{\eta}{\eta_0} = 1 + [\eta]c + k_1[\eta]^2c^2 \tag{2}$$

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and Kraemer[3]:

$$\frac{1}{c} \ln \left[\frac{\eta}{\eta_0} \right] = [\eta] - k_1'[\eta]^2 c. \tag{3}$$

Equation (2) is evidently a truncated version of eq. (1). Expansion of the logarithm in eq. (3) and neglect of higher terms in the resulting Taylor series leads to the conclusion that plots of η_{sp}/c and $1/c \ln \eta/\eta_0$ should extrapolate to the same intercept ($[\eta]$) at zero c. If the data points can indeed be represented by eqs. (2) and (3), it is also readily shown that

$$k_1 + k_1' = 0.5. \tag{4}$$

The conventional measurement of $[\eta]$ involves a double extrapolation of eqs. (2) and (3), with the expectation that the intercepts will coincide closely enough to warrant use of a mean value for $[\eta]$ and that the slopes of the relationships will conform to the sum indicated by eq. (4). This data treatment anticipates that the experimental values of η_{sp}/c and $1/c \ln \eta/\eta_0$ will be accurately linear in c. The resulting estimations of $[\eta]$ and of the Huggins constant k_1 may be inaccurate to the extent that truly curvilinear experimental relations are forced into rectilinear forms for computational convenience.

Solomon and co-workers[4,5] and others have shown that $[\eta]$ can be deduced from a single value of η/η_0 at given c, if the linearity implied in eqs. (2) and (3) is indeed applicable to the experimental points. It seems, however, that single-point equations for $[\eta]$ are reliable in practice only for low-concentration data in particular polymer–solvent combinations in which the Huggins' constant k_1 is not far from 0.33.[6,7] This conclusion illustrates the widely perceived fact that neither the Huggins nor the Kraemer equations are strictly valid at most practical concentrations, since they are truncated versions of actual power series.[8]

It might appear that the difficulties cited could be avoided by confining experimental concentrations to very low values such that the higher terms in the respective power series are indeed negligible. This is, however, not a generally practical procedure. The experimental uncertainty in the η/η_0 ratio becomes unacceptably large, and the plot of η_{sp}/c against c usually exhibits an inflection at sufficiently low c.[9,10]

A number of authors have recognized these reasons for the failure of experimental data always to conform to expectations. Extrapolation methods have been suggested based on power series relations such as those in eqs. (1) and (5):

$$\frac{1}{c} \ln \left[\frac{\eta}{\eta_0} \right] = [\eta] - k_1'[\eta]^2 c - k_2'[\eta]^3 c^2 - \ldots . \tag{5}$$

Heller[11] begins with these equations, for example. His object is, however, to produce a graphically useful result, and this necessitates a final expression, for $\frac{1}{2}\{(c/\eta_{sp}) + [c/\ln(\eta/\eta_0)]\}$ in this case, which is linear in c. That is to say, the infinite series relations are eventually reduced in order to

provide a rectilinear relation with two graphically accessible parameters (slope and intercept). This representation may have some advantages over the conventional bilinear extrapolation of eqs. (2) and (3).[11] It is clear, however, that the use of truncated pseudolinear forms of what is probably essentially a curvilinear relation may result in differences in slopes and intercepts estimated from the same data by the different methods, even though all the approximate relationships are mathematically valid in the limits of high dilution. This conclusion is illustrated by Bohdanecky.[12]

The same problem is inherent in all attempts to improve the methods for estimating (η) by graphic extrapolation. Sakai's[13] review of various extrapolation procedures indicates that equations with only one slope constant are unlikely to fit data from all polymer–solvent combinations.

Maron and Reznik[14] have recently considered the problem of estimating $[\eta]$ and k_1. Their recommendations were used in the present work as a departure point for comparisons of two-parameter and three-parameter estimation methods. These authors begin with the forms

$$\frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2 c + k_2[\eta]^3 c^2 \tag{1a}$$

and

$$\frac{1}{c} \ln\left[\frac{\eta}{\eta_0}\right] = \frac{1}{c} \ln \eta_r = [\eta] - k_1'[\eta]^2 c - k_2'[\eta]^3 c^2. \tag{5a}$$

In this article the graphic solution[14] of eqs. (1a) and (5a) is compared to results obtained by nonlinear regression analysis for best-fit values of $[\eta]$ and the other constants in the same equations. Computer-assisted regression analysis provides a direct solution to these equations. Graphically useful solutions, on the other hand, must assume certain relations between the slope parameters to reduce the numbers of constants on the rhs of each equation to two.

Equations (1a) and (5a) are infinite power series truncated after the c^2 terms, as written. Inclusion of more terms in the series would prevent simplification of these relations to graphically useful forms. Regression analyses with equations with more than the three parameters listed would likewise probably not be efficient. It is usually not convenient to measure solution viscosities at more than five or six concentrations, and a data analysis which minimizes residual squared deviations can be meaningful only if the number of fitted parameters is exceeded by the number of independent data points.

The work reported here proceeds from the generally accepted premise that eqs. (1a) and (5a) are superior representations of dilute solution viscosity data. The results are novel in that this is the first instance to our knowledge in which these relations are solved directly without the use of assumptions to reduce the equations to two-parameter forms for graphic solution.

ESTIMATION OF PARAMETERS

By expanding the logarithmic term in eq. (5a) and comparing with eq. (1a), Maron and Reznik[14] deduce that the four slope constants in these two equations should be related by eqs. (4) and (6):

$$k_2 + k_2' = k_1 - \frac{1}{3}. \tag{6}$$

It can then be shown that

$$\frac{\eta_{sp} - \ln \eta_r}{c^2} = \frac{[\eta]^2}{2} + \left[k_1 - \frac{1}{3} \right][\eta]^3 c \tag{7}$$

and the lhs of eq. (7) can be plotted against c to provide a rectilinear relation from which $[\eta]$ and k_1 can be estimated. Equation (7) depends on the validity of eqs. (4) and (6). The quadratic eqs. (1a) and (5a) have been reduced to two-parameter forms to provide a graphically useful solution.

The experimental data in this article were fitted to eq. (7) by computer assisted linear least-squares adjustment of the slope and intercept, in place of a direct graphic solution. We wish to compare the results of the linear least-squares fit to eq. (7) to the nonlinear regression analysis fit of the data directly to eqs. (1a) and (5a). The most convenient parameter for comparison of these procedures is provided by the multiple correlation coefficient[15] R^2. R^2 is defined as follows:

$$R^2 = \Sigma(\hat{Y}_i - \bar{Y})^2 / \Sigma(Y_i - \bar{Y})^2 \tag{8}$$

where the summations are in i over all the data; $\bar{Y}$ is the mean value of Y_i; and $\hat{Y}_i$ is the value of Y_i estimated by the regression equation. Perfect prediction would evidently result in $\hat{Y}_i = Y_i$ and $R^2 = 1$. The multiple correlation coefficient is a normalized variate ($0 \leq R^2 \leq 1$) and reflects the fraction of the variation in the dependent variable which is accounted for by the regression equation. The regression equation is better the closer R^2 is to unity (provided the number of independent data values exceeds the number of adjustable parameters).

Equations (1a) and (5a) were applied separately to the experimental data by adjusting $[\eta]$ and the two k parameters in each relation to maximize R^2. APL programs[16] were written to perform these manipulations. Copies of the programs are available from the authors. The procedure reported seems to involve the most direct and rigorous application of eqs. (1a) and (5a). It has not been possible to apply this method before the recent advent of concise computer-assisted data-fitting techniques. The previous workers mentioned here who used the less exact two-parameter graphic solutions to the three-parameter equations were forced to such means for lack of more efficient tools.

The results given here illustrate the application of the new, direct solutions of the three-parameter equations and also, incidentally, provide estimates of the efficiencies of the various graphically useful approximations in different polymer–solvent mixtures.

Dilute Solutions

We first compare the direct nonlinear regression fit to eqs. (1a) and (5a) with the graphic solution through eq. (7). Table I summarizes results of the application of these three equations to data measured with cyclohexanone solutions of poly(vinyl chloride) (PVC). The three commercial PVC polymers studied in detail were Rucon B-29, Opalon 650, and Geon 101EP. Molecular weight distributions of these polymers have been described elsewhere.[17]

The PVC specimens used for solution viscosity measurements were taken from samples which had been used for a series of melt rheology measurements. The same compound was examined after various thermal histories, as shown in the table. The different heat histories (details of which are not relevant to this article) account for the variations recorded in $[\eta]$ for different specimens of the same material. Each PVC was initially stabilized with 4 wt-% of proprietary Ba-Cd-Zn liquid stabilizers. The same batch of distilled cyclohexanone with a boiling range of 155–156°C was used in all measurements. Solution viscosities were measured at 30°C at five concentrations, using Ubbelohde viscometers.[18] The most concentrated solutions contained about 0.1 g/dl polymer.

Table I lists $[\eta]$, slope constants, and the multiple correlation coefficients R^2. Although the latter parameters are given to four decimal places, rounding-off results in R^2 being given as unity in several cases. This indicates an apparent exact fit of the regression equation to the experimental data. However, this perfect situation would doubtlessly not obtain if data from more than five concentrations had been fitted to the same equations.

The $[\eta]$ values in Table I which were calculated from eqs. (1a) and (5a) agree very well. These values were obtained, as noted, by statistical manipulations which minimized the differences between a regression equation and the experimental data. Such best-fit relations may not necessarily be best for extrapolation.[13] As a general rule, the statistical exercise optimizes on the results in the experimental range and has no necessary relation to values outside this range. The present results can, however, be extrapolated to estimate the $[\eta]$ intercept with some confidence since both curvilinear regression equations have some foundation in theory, both give coincident intercepts, and both account for better than 99% (R^2) of the data scatter at experimental concentrations.

The values of $[\eta]$ from the linear least-squares fits to Maron and Reznik's eq. (7) do not agree quite as closely with the preceding two estimates. The former technique seems capable in this case, however, of providing a convenient graphic estimate of $[\eta]$ which is reliable enough to two decimal places for characterization of polymer $\bar{M}_v$. The built-in assumptions, eqs. (4) and (6), of this and all other two-parameter approximations to eqs. (1a) and (5a) render such models less suitable for studies of polymer–solvent interactions than for measurement of viscosity-average molecular weights.

TABLE I

PVC–Cyclohexanone Dilute Solution Viscosities

| Sample | | Equation (1a) | | | | Equation (5a) | | | | Equation (7) | | | |
Code	Description	$[\eta]$, dl/g	k_1	k_2	R^2	$[\eta]$, dl/g	k_1'	k_2'	R^2	$[\eta]$, dl/g	Slope, dl³/g³	k_1	R^2
A1	Rucon B26 polymer	0.599	0.273	0.092	0.9990	0.598	0.207	-0.078	0.9964	0.595	-0.0008	0.332	0.0866
A2	A1 plus stabilizer	0.594	0.284	0.152	0.9991	0.594	0.204	-0.071	0.9967	0.591	-0.0015	0.326	0.3078
A3	A2 compression molded	0.556	0.324	0.040	0.9968	0.556	0.169	-0.025	0.9881	0.556	-0.0011	0.327	0.1251
A4	A2 after melt flow measurements	0.541	0.590	-0.324	0.9980	0.544	0.012	0.229	0.9911	0.557	-0.0008	0.328	0.0170
B1	Opalon 650 polymer	1.020	0.470	-0.085	0.9998	1.029	0.098	0.039	0.9993	1.047	-0.0085	0.326	0.2032
B2	B1 plus stabilizer	1.060	0.114	0.098	0.9993	1.049	0.309	-0.109	0.9985	1.022	-0.0552	0.279	0.8562
B3	B2 compression molded	0.934	0.410	-0.008	1.0	0.937	0.118	0.099	0.9998	0.944	0.137	0.348	0.9251
B4	B2 after melt flow measurements	0.893	0.570	-0.061	0.9999	0.901	0.008	0.081	0.9996	0.919	0.0494	0.397	0.8625
C1	Geon 101EP polymer	1.139	0.334	0.045	0.9995	1.172	0.206	0.053	0.9959	1.046	0.1292	0.457	0.7611
C2	C1 plus stabilizer	1.079	0.392	0.021	1.0	1.080	0.145	0.013	1.0	1.083	0.0143	0.346	0.9779
C3	C2 compression molded	1.136	0.223	0.085	0.9930	1.126	0.222	0.031	0.9933	1.110	-0.0024	0.335	0.2662
C4	C2 hot milled and extruded	1.088	0.358	0.010	1.0	1.089	0.156	0.015	0.9999	1.092	-0.0002	0.333	0.4189
C5	C2 hot milled	1.124	0.385	0.010	1.0	1.125	0.130	-0.001	0.9998	1.129	0.0255	0.351	0.9504
C6	C2 hot milled and compression molded	1.131	0.224	0.072	0.9997	1.126	0.240	0.075	0.9989	1.113	-0.0225	0.308	0.7474
C7	C2 after melt flow measurements	1.081	0.297	0.044	0.9987	1.078	0.185	0.073	0.9948	1.073	0.0068	0.327	0.3140

Ideally, the sum of k_1 and k_1' should be close to 0.5, eq. (4). The mean (μ) of the initial slopes tabulated from eqs. (1a) and (5a) calculations is 0.509, which is close to the expected value. The confidence limits of this mean are such, however, that $0.453 \leq \mu \leq 0.565$ (95%).

The PVC–cyclohexanone data conform to eq. (4) within the limits given, but the relation expressed by eq. (6) is not effectively satisfied. As a result, the k_1 values assessed by the method of Maron and Reznik are not comparable to those obtained by direct fitting of eq. (1a) to the same experimental data.

The multiple correlation coefficients R^2 from regression analyses on eq. (7) are lower than the corresponding parameters obtained by applying eqs. (1a) and (5a). This is probably because eq. (7) requires accurate measurement of the difference between η_{sp} and $\ln \eta_r$. Both these quantities are small and their difference may approach the magnitude of the experimental error.

The data in Table II compare results of nonlinear regressions on eqs. (1a) and (5a) with applications of the Huggins, eq. (2), Kraemer, eq. (3), and Maron and Reznik, eq. (7), relations. The latter three equations were fitted to the data with a linear least-squares program instead of the more convenient but more subjective graphic solution. The raw data were obtained in our laboratory with various polymer–solvent combinations at 25°C. All dilute solution viscosities were measured at six concentrations. Except for the polystyrene–butanone solution, $[\eta]$ values from the Huggins, Kraemer, and Maron and Reznik representations seem to be mutually consistent and slightly different from the intrinsic viscosities obtained from eqs. (1a) and (5a). The latter equations presumably provide the definitive values of $[\eta]$ because the relations used involve fewer assumptions. The three rectilinear relations of eqs. (2), (3), and (7) can all be accommodated in eqs. (1a) and (5a) with appropriate values of the k parameters. The reverse case is not true, however. A truly curvilinear situation cannot be handled by eqs. (2) or (3) and is accommodated by eq. (7) only with the proviso that eqs. (4) and (6) are valid. In addition, eqs. (1a) and (5a) account better for all the experimental data (R^2 is higher).

As in Table I, the choice of data-handling method affects the slope constants more than the $[\eta]$ intercepts. Equation (6) is not supported by the experimental values of k_1, k_2, and k_2' from data fitting to eqs. (1a) and (5a). The Huggins constant k_1 is assigned rather different values by data fitting to eqs. (2), (1a), and (7).

Moderately Concentrated Solutions

Weissberg, Simha, and Rothman[19] have reported solution viscosities of polystyrene fractions over a very wide concentration range in several solvents. These data are used here to compare the intercept and slope estimates from the various techniques discussed above.

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TABLE II
Dilute Solution Data (25°C)

Polymer Solvent	Dow Styron 683 polystyrene dioxane	Anionic polystyrene (M = 61,000) 2-butanone	Vistanex L-80 poly-isobutene toluene	Vistanex LM-MS poly-isobutene cyclohexane	Opalon 650 poly(vinyl chloride) tetra-hydrofuran
Huggins Equation, eq. (2):					
$[\eta]$, dl/g	0.723	0.200	1.966	0.464	1.052
k_1	0.400	0.443	0.555	0.328	0.350
R^2	0.9949	0.9985	0.9982	0.9605	0.9975
Kraemer equation, eq. (3):					
$[\eta]$, dl/g	0.725	0.200	2.030	0.463	1.049
k_1'	0.125	0.080	0.089	0.162	0.144
R^2	0.9704	0.9594	0.9988	0.8951	0.9910
$k_1 + k_1'$	0.525	0.523	0.644	0.490	0.494
Equation (1a):					
$[\eta]$, dl/g	0.702	0.200	2.042	0.455	1.081
k_1	0.588	0.461	0.389	0.496	0.252
k_2	−0.184	−0.071	0.086	−0.245	0.073
R^2	0.9994	0.9986	1.0	0.9664	0.9999
Equation (5a):					
$[\eta]$, dl/g	0.709	0.200	2.039	0.456	1.027
k_1'	0.009	0.045	0.102	0.059	0.214
k_2'	0.135	0.140	−0.009	0.169	−0.055
R^2	0.9956	0.9651	1.0	0.9063	0.9999
k_1 (eq. (1a)) + k_1' (eq. (5a))	0.597	0.506	0.491	0.555	0.466
$k_1 - {}^1/_3 - k_2 - k_2'$ (eq. (6))	0.304	0.059	−0.021	0.239	0.047
Equation (7):					
$[\eta]$, dl/g	0.727	0.200	2.033	0.464	1.059
k_1	0.359	0.421	0.407	0.319	0.323
R^2	0.4583	0.9639	0.9986	0.0529	0.5504

The results of Weissberg and co-workers extend to much higher values of solution concentration than 1.0–1.5 g/dl which is the normal upper limit for estimates of $[\eta]$ and Huggins' constant. These authors estimated $[\eta]$ and k_1 by fitting least squares lines to the data (as η_{sp}/c and c) over concentrations in which the deviations from linearity appeared to be random. That is to say, the Huggins equation, eq. (2), was used, in the concentration range in which it seemed to be applicable.

The $[\eta]$, k_1, and concentration limits for eq. (2) given by Weissberg et al. are recorded in the following tables. Also included are intercepts and slope constants estimated by the various relations considered earlier in this article. In the latter case we have used blocks of experimental results extending from a common lowest concentration to progressively higher upper concentration limits. This provides an evaluation of the applicability of the

TABLE III
Polystyrene ($M = 58,000$) in Toluene at 30°C and 48.2°C[a]

	30°C				48°C		
Solution concentration:							
No. concentrations	6	10	15	24	6	12	18
Lowest concentration, g/dl	0.0778	0.0778	0.0778	0.0778	0.1978	0.1978	0.1978
Highest concentration, g/dl	0.4866	1.1699	2.0659	5.6446	1.2547	2.9601	4.9372
Huggins equation, eq. (2):							
$[\eta]$, dl/g	0.369	0.369	0.368	0.362	0.324	0.325	0.323
k_1	0.314	0.328	0.344	0.402	0.442	0.421	0.437
R^2	0.9730	0.9963	0.9965	0.9975	0.9950	0.9982	0.9993
Kraemer equation, eq. (3):							
$[\eta]$, dl/g	0.369	0.368	0.368	0.364	0.325	0.326	0.326
k_1'	0.183	0.167	0.155	0.124	0.094	0.118	0.116
R^2	0.9255	0.9878	0.9900	0.9877	0.9259	0.9872	0.9970
k_1 (eq. (2)) + k_1' (eq. (3))	0.497	0.495	0.498	0.526	0.536	0.538	0.552
Equation (1a):							
$[\eta]$, dl/g	0.370	0.369	0.370	0.368	0.325	0.325	0.325
k_1	0.275	0.309	0.284	0.338	0.397	0.406	0.414
k_2	0.189	0.041	0.081	0.034	0.098	0.015	0.014
R^2	0.9736	0.9965	0.9984	0.9996	0.9953	0.9983	0.9995
Equation (5a):							
$[\eta]$, dl/g	0.370	0.369	0.369	0.368	0.325	0.325	0.326
k_1'	0.229	0.190	0.200	0.165	0.116	0.106	0.119
k_2'	-0.223	-0.053	-0.063	-0.023	-0.048	0.012	-0.002
R^2	0.9281	0.9890	0.9960	0.9981	0.9272	0.9879	0.9970
k_1 (eq. (1a)) + k_1' (eq. (5a))	0.514	0.499	0.484	0.503	0.515	0.512	0.533
Equation (7):							
$[\eta]$, dl/g	0.365	0.367	0.367	0.366	0.325	0.327	0.328
k_1	0.398	0.336	0.333	0.341	0.404	0.367	0.357
R^2	0.0293	0.0006	0.0002	0.1663	0.8624	0.8158	0.8585

[a] At 30°C data are linear to 1.4 g/dl with $[\eta] = 0.369$ g/dl and $k_1 = 0.322$.[19] At 48.2°C data are linear to 5 g/dl with $[\eta] = 0.324$ g/dl and $k_1 = 0.437$.[19]

TABLE IV
Polystyrene ($M = 146,000$) in 90 Butanone/10 Isopropanol at 30°C[a]

Solution concentration:				
No. concentrations	6	8	15	27
Lowest concentration, g/dl	0.0555			
Highest concentration, g/dl	0.4969	1.0013	3.1579	8.5624
Huggins equation, eq. (2):				
$[\eta]$, dl/g	0.322	0.323	0.321	0.274
k_1	0.609	0.567	0.615	1.282
R^2	0.9603	0.9904	0.9959	0.9726
Kraemer Equation, eq. (3):				
$[\eta]$, dl/g	0.323	0.326	0.327	0.328
k_1'	−0.055	0.002	0.046	0.048
R^2	0.1571	0.0004	0.7229	0.9740
k_1 (eq. (2)) + k_1' (eq. (3))	0.553	0.569	0.661	1.330
Equation (1a):				
$[\eta]$, dl/g	0.323	0.323	0.325	0.331
k_1	0.498	0.605	0.505	0.525
k_2	0.630	−0.115	0.119	0.350
R^2	0.9622	0.9906	0.9985	0.9997
Equation (5a):				
$[\eta]$, dl/g	0.324	0.323	0.326	0.327
k_1'	0.045	−0.154	0.020	0.045
k_2'	−0.562		0.028	0.001
R^2	0.1876	0.1271	0.7418	0.9743
k_1 (eq. (1a)) + k_1' (eq. (5a))	0.533	— 0.451	0.525	0.570
Equation (7):				
$[\eta]$, dl/g	0.305	0.252	0.285	0.317
k_1	1.170	2.410	0.807	0.535
R^2	0.6072	0.2253	0.3395	0.9843

[a] Data are linear to 1 g/dl with $[\eta] = 0.323$ g/dl and $k_1 = 0.572$.[19]

various techniques for estimating $[\eta]$ and the slope constants as the experimental solution viscosity functions deviate more and more from linearity in solution concentration.

The extensive data of Weissberg and co-workers[19] include experimental results at two temperaures for three polystyrene fractions ($M = 58,000$, 146,000, and 600,000) in toluene, 2-butanone, and a 90/10 mixture of butanone and isopropanol.

As expected, the data which conform most closely to the expected linearity of the forms in eqs. (2) and (3) are those for the lowest molecular weight polymer ($M = 58,000$) in the best solvent (toluene). Table III records the $[\eta]$ and k_1 values of Weissberg and co-workers and their estimates that η_{sp}/c was linear in c up to 1.4 g/dl at 30°C and to 5 g/dl at 48.2°C. Within these concentration limits, all five data representations

TABLE V

Polystyrene (M = 600,000) in 90 Butanone/10 Isopropanol at 30°C and 48.2°C[a]

	30°C		48.2°C	
Solution concentration:				
No. concentrations	6	9	6	8
Lowest concentration, g/dl	0.1081	0.1081	0.2247	0.2247
Highest concentration, g/dl	1.247	1.9952	1.3753	2.0308
Huggins equation, eq. (2):				
$[\eta]$, dl/g	0.778	0.739	0.791	0.744
k_1	0.744	0.961	0.717	0.943
R^2	0.9930	0.9906	0.9671	0.9804
Kraemer equation, eq. (3):				
$[\eta]$, dl/g	0.809	0.813	0.851	0.847
k_1'	0.017	0.027	0.065	0.056
R^2	0.9470	0.9254	0.8440	0.9048
k_1 (eq. (2)) + k_1' (eq. (3))	0.762	0.989	0.782	0.999
Equation (1a):				
$[\eta]$, dl/g	0.811	0.807	0.911	0.862
k_1	0.493	0.579	0.088	0.410
k_2	0.240	0.247	0.493	0.321
R^2	1.0	0.9999	0.9963	0.9971
Equation (5a):				
$[\eta]$, dl/g	0.808	0.806	0.876	0.860
k_1'	0.013	−0.002	0.164	0.099
k_2'	0.003	0.018	−0.073	−0.024
R^2	0.9496	0.9888	0.9379	0.9387
k_1 (eq. (1a)) + k_1' (eq. (5a))	0.506	0.577	0.252	0.509
Equation (7):				
$[\eta]$, dl/g	0.802	0.800	0.808	0.799
k_1	0.531	0.541	0.511	0.537
R^2	0.9960	0.9985	0.5123	0.7862

[a] At 30°C data are not linear and $[\eta]$ estimated as 0.771 g/dl.[19] At 48.2°C data are not linear and $[\eta]$ estimated as 0.874 g/dl.[19]

produce the same $[\eta]$ to within 0.002 g/dl. (The original concentration and viscosity data are given to four decimal places.) Equation (7) gives the lowest multiple correlation coefficient, but the $[\eta]$ values derived from this representation of the data are not seriously different from the figures given by the other techniques. This is because R^2 by its definition is a measure of the usefulness of the terms other than the intercept in the model regression equation.[15] R^2 is a measure of the goodness of fit to the experimental points, as reflected in the slope constants in the power series equation in concentration. This particular polymer–solvent combination is close to "ideal" in behavior, and so the linear Huggins and Kraemer equations account for the observations as well as the curvilinear expressions,

Polystyrene molecular weight	50,000	50,000	600,000	600,000	600,000	600,000
Solvent	toluene	toluene	90 butanone 10 isopropanol	butanone	butanone	toluene
Temperature, °C	30	48.2	30	30	48.2	30
No. concentrations	25	18	9	17	12	20
Lowest concentration, g/dl	0.0778	0.1978	0.1081	0.0541	0.2493	0.0175
Highest concentration, g/dl	5.9268	4.9732	1.9952	4.9516	5.2624	3.3969
Equation (1b):						
$[\eta]$, dl/g	0.369	0.326	0.812	1.014	0.968	2.051
k_3	0.307	0.391	0.434	0.534	0.584	0.359
k_4	0.055	0.039	0.253	0.007	0.014	−0.001
k_5	−0.007	−0.010	−0.026	0.027	0.030	0.004
R^2	0.9997	0.9995	1.0	0.9999	1.0	0.9998
Equation (5b):						
$[\eta]$, dl/g	0.369	0.325	0.809	1.026	0.997	2.050
k_3'	0.184	0.105	0.021	0.062	0.061	0.158
k_4'	−0.049	0.019	−0.016	0.006	0.003	−0.019
k_5'	0.009	−0.009	0.013	−0.001	−0.001	0.001
R^2	0.9989	0.9972	0.9946	0.9900	0.9967	0.9984
$[\eta]$ from eqs. (1a) and (5a)	0.370	0.325	0.810	1.020	1.010	2.047

and R^2 is essentially the same for the corresponding relations in eqs. (2)/(1a) and (3)/(5a). Somewhat surprisingly, however, this does not mean that the extra terms in eqs. (1a) and (5a) have zero values for the respective coefficients k_2 and k_2'.

The data in Table IV are for 146,000 molecular weight polystyrene at 30°C in the marginal solvent mixture of 90 butanone/10 isopropanol. Curvature of η_{sp}/c plots is more pronounced than in the case summarized in Table III. Equation (7) is clearly inadequate in this instance and gives unreliable estimates of $[\eta]$ and k_1.

The raw data for 600,000 molecular weight polystyrene in the mixed butanone–isopropanol solvent were not linear in terms of η_{sp}/c and c over any concentration range.[19] As would be expected then, the $[\eta]$ extrapolations are affected to some extent by the estimation method. We see in Table V that the intercepts from the Huggins and Kraemer equations do not match well and the sums of the limiting slope parameters k_1 and k_1' are not near the orthodox value of $1/2$. It is also not surprising that the extended series forms of eqs. (1a) and (5a) seem to be more applicable to these data.

Use of Extended Power Series

Extension of the power series forms of eqs. (1a) and (5a) to include more terms would be expected to represent experimental data over an even wider concentration range. Equations (1b) and (5b) are the corresponding four parameter forms:

$$\frac{\eta_{sp}}{c} = [\eta] + k_3[\eta]^2 c + k_4[\eta]^3 c^2 + k_5[\eta]^4 c^3 \qquad (1b)$$

$$\frac{1}{c} \ln \eta_r = [\eta] - k_3'[\eta]^2 c - k_4'[\eta]^3 c^2 - k_5'[\eta]^4 c^3. \qquad (5b)$$

VI
Power Series

600,000 toluene	146,000 90 butanone 10 isopropanol	146,000 90 butanone 10 isopropanol	146,000 butanone	146,000 butanone	146,000 toluene	146,000 toluene
48.2	30	48.2	30	48.2	30	48.2
12	27	25	37	20	30	25
0.1414	0.0555	0.2501	0.0969	0.2505	0.0433	0.1360
3.7971	8.5624	8.3860	8.8312	7.0772	9.3280	9.1760
1.984	2.345	0.360	0.448	0.388	0.707	0.620
0.332	−0.263	0.325	0.349	0.318	0.351	0.313
0.006	0.023	0.086	0.079	0.157	0.003	0.016
0.004	−0.006	0.021	0.010	−0.009	0.005	0.002
1.0	0.3844	0.9996	1.0	0.9998	0.9999	0.9999
1.975	0.503	0.355	0.447	0.386	0.707	0.610
0.164	0.781	0.127	−0.131	0.134	0.158	0.161
−0.021	−0.381	−0.031	−0.27	−0.048	−0.020	−0.021
0.001	0.052	0.003	0.003	−0.009	0.001	0.001
0.9998	0.9883	0.9910	0.9981	0.9941	0.9995	0.9943
1.973	0.323	0.350	0.445	0.384	0.703	0.620

The data of Weissberg and co-workers[19] are again particularly suitable to test these expressions since the number of concentrations is always great enough not to saturate the regression equation.

Table VI shows that the inclusion of more extended forms of the power series covers the available solution viscosity data up to 9% (w/v) in some cases. The multiple regression coefficient R^2 is almost always >0.99, indicating that the power series forms, eq. (1), are correct in principle. The [η] extrapolations do not coincide as well as they do when estimated only from dilute concentrations. The behavior of 146,000 molecular weight polystyrene data in butanone/isopropanol is anomalous in Table VI, for reasons which are not clear.

DISCUSSION

Ibrahim and Elias[3] have shown that different values of [η] can be obtained from Huggins, eq. (2), and Kraemer, eq. (3), plots even when the former equation is obeyed exactly, if the Huggins constant is large. This discrepancy stems from neglect of higher terms in the Taylor series expansion for ln η_r in the Kraemer relation.

It was of interest to consider how closely [η] values from eqs. (1a) and (5a) matched, since these relations are simply extensions of the Huggins and Kraemer equations. The data listed in Table I were used for this comparison.

We have assumed in this case that the differences between [η] values calculated from eqs. (1a) and (5a) are normally distributed. The 95% confidence limits for the mean difference (d_1) is such that $-0.009 \leq d_1 \leq 0.001$. The [$\eta$] values from the two equations are not significantly different (for the PVC results in Table I), since zero difference is within the estimated interval. Applications of similar analyses to the differences

between $[\eta]$ values from Maron and Reznik's eq. (7) and those from either eq. (1a) or (5a) gives a larger variance of distribution of differences; 95% confidence limits are still such as to include zero difference.

This report is based on the well-known assumption that the viscosity of dilute polymer solutions can be expressed accurately as a virial equation in concentration. For reasons mentioned, it is not generally practical or convenient for most purposes to extend this relation beyond the cubic power in concentration. Various attempts have been made to evaluate the intercept and slope constants in such expressions graphically. Two such procedures mentioned in this article are those of Heller[11] and Maron and Reznik,[14] but our conclusions appear to apply equally to all such methods.

Any graphically useful technique must involve approximation of the three-parameter equation (in this case) with a two-parameter solution. Assumptions are therefore involved concerning the relations between some of the parameters in the initial power series form. These assumptions are often valid in certain cases, but experience does not seem to inindicate a general applicability of any such particular solution. The double extrapolation of the Huggins and Kraemer equation forms is a special case of such graphically useful approximations to solutions to a nonlinear equation. In this case, the parameters k_2 and k_2' in eqs. (1a) and (5a), respectively, are each assigned zero value.

We have shown here that direct solution of eqs. (1a) and (5a) by nonlinear regression analysis of experimental data confirms the expectation that much of the difficulty with abbreviated forms of these relations can be removed. This straightforward solution to the problem is practical only recently, since it relies on computer-assisted calculations. The various two-parameter approximations to the solution of eqs. (1a) and (5a) must necessarily be less widely applicable than the procedure used here.

The graphic estimates may nevertheless be quite adequate for estimates of $[\eta]$ for most purposes. They seem to be less reliable for calculation of Huggins' constants or other slope parameters, since such constants reflect the approximation of a chord to a real curve.

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