

Programmed Polymer Light-Scattering Data

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Synopsis

An ALGOL computer program has been devised to manipulate light-scattering data from the Brice-Phoenix photometer. The input consists of experimental values of the galvanometer deflections and filter factors used for each concentration c and angle of measurement θ . These are transformed to the appropriate variables in the fundamental equation including the particle scattering factor, viz: $c/Q_\theta = (W/K^*)\bar{M}_w^{-1}[1 + (16/3) \times \pi^2 n_i^2 \lambda^2 \langle S^2 \rangle \sin^2(\theta/2)] + (W/K^*)2A_2c + (W/K^*)3A_3c^2$ in which Q_θ is a corrected form of the Rayleigh ratio and (W/K^*) is a composite constant term for the instrument and polymer-solvent system. By writing \bar{X}_{ij} for the variable c/Q_θ at θ_i and c_j , a function X is found by least squares to fit \bar{X}_{ij} , thus $X = l + m \sin(\theta/2) + nc_j + bc_j^2$. The equations arising from minimizing $\sum_{i=1}^K \sum_{j=1}^L (X_{ij} - \bar{X}_{ij})^2$ are solved by the computer to yield the best-fitting coefficients l , m , n , and b . These can then be related simply to the molecular weight, root-mean-square radius of gyration, second and third virial coefficients, respectively. The final portion of the program is designed to check the fit of these coefficients. It yields a table of the differences between all experimental c/Q_θ values and the corresponding ones obtained by inserting the derived l , m , n , and b into the fundamental equation. The procedure has been tested satisfactorily by using a well-standardized sample of polystyrene in toluene at 30°C. and a wavelength of 436 m μ .

INTRODUCTION

Determination of the weight-average molecular weight \bar{M}_w is the principal object of light-scattering measurements on polymer solutions. Moreover, by appropriate manipulation of the data, additional information on dimensions and interactions may be derived. Computer techniques are beginning to play a role in polymer chemistry,¹⁻³ and in this paper it is our intention to demonstrate the utility of a simple computer program designed to yield all the normally required quantities from an input of experimental readings alone. The approach is directed to the case of a scan of the angular distribution of intensity at a series of concentrations wherein the calculations and Zimm plot are tedious rather than difficult. We note in this respect a recent communication by van Wilk and Staverman⁴ illustrating the resolution of a possible difficulty in a Zimm plot. For the particular system (as well as some others⁵) the conventional plot with $\sin^2(\theta/2) + kc$ as abscissa yielded a confusing involuted grid. This was unravelled satisfactorily by assigning a negative value to the arbitrary constant k . It

will be seen that such a difficulty does not arise in our procedure, as the coordinates are treated statistically and, indeed, the Zimm grid is not plotted.

The ALGOL (algorithmic language) program, which appears as an appendix, is written for use with the KDF9 (English Electric) computer, and the measurements appertain to the Brice-Phoenix light-scattering photometer series 2000, both of which enjoy widespread use. No entirely novel conceptual developments are invoked. In this connection we note that Debye et al.⁶ deployed a variational method of least squares combined with a power development to obtain the radius of gyration of polystyrene. Furthermore Leblanc⁷ has compiled an excellent detailed account of how measurements with the Brice-Phoenix machine are treated arithmetically in order to obtain \bar{M}_w . Our procedure is designed to have a wider (and clearly more time-saving) potential. However, in view of these peripheral publications, our attention will be confined primarily to considerations of (a) numerical manipulation needed, (b) presentation of the program to accomplish this, and (c) experimental verification of the method.

UNITS

Fundamental c.g.s. units are employed throughout, viz: concentration c in g./ml., specific refractive index increment \bar{n} in ml./g., wavelength *in vacuo* λ in cm., angle θ in degrees, second virial coefficient A_2 in g.⁻² cm.³ mole, third virial coefficient A_3 in gm.⁻³ cm.⁶ mole and root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ in cm.

THE RAYLEIGH RATIO

The Rayleigh ratio R_θ for θ° may be written in the corrected form suggested by Tomimatsu and Palmer,⁸ which we abbreviate to

$$R_\theta = WYZ \quad (1)$$

where

$$W = \frac{TDan_1^2(R_w/R_c)(r/r')}{1.049\pi h} \cdot \left[\frac{1}{(1-R)^2(1-4R^2)} \right] \quad (2)$$

$$Y = \sin \theta / (1 + \cos^2 \theta) \quad (3)$$

and

$$Z = \left[\left(\frac{fG_\theta}{fG_0} \right)_{\text{soln}} - \left(\frac{fG_\theta}{fG_0} \right)_{\text{solv}} \right] - 2R \left[\left(\frac{fG_{180-\theta}}{fG_0} \right)_{\text{soln}} - \left(\frac{fG_{180-\theta}}{fG_0} \right)_{\text{solv}} \right] \quad (4)$$

In eq. (2) the terms are given in the Brice-Phoenix manual⁹ and will be familiar to users of the instrument. It is pertinent only to emphasize firstly, that R_c , R_w , and R have no connection with R_θ and secondly, that, in common with others,¹⁰ we find it imperative to measure the value of r/r' before each experiment even when working with similar systems. In

eq. (3) $\sin \theta$ is introduced to correct for the volume change on viewing the solution at different angles, while $(1 + \cos^2 \theta)$ accounts for the state of polarization of the scattered light.

In eq. (4) it will be noted that only angles supplementary to each other can be used. When no neutral filters are inserted $f = 1$. Otherwise the symbol f denotes the reciprocal of the transmittance of the filter or the product of such reciprocals when more than one filter is incorporated. G is the galvanometer reading.

FUNDAMENTAL RELATIONSHIPS

The predetermined light-scattering constant for a particular polymer-solvent system is K^* defined by

$$K^* = (2\pi^2 n_1^2 \bar{n}^2) / \lambda^4 N_A \quad (5)$$

where \bar{n} is the specific refractive index increment, n_1 is the refractive index of the solvent, and the other terms have their customary connotation. Experimentally, values of K^*c/R_θ are required for each angle θ and concentration c . If the measured product YZ is abbreviated to Q_θ , then

$$K^*c/R_\theta \equiv (K^*/W)(c/Q_\theta) \quad (6)$$

The dependences of K^*c/R_θ on concentration and angle are:

$$\lim_{\theta=0} (K^*c/R_\theta) = \bar{M}_w^{-1} + 2A_2c + 3A_3c^2 \quad (7)$$

and

$$\lim_{c=0} (K^*c/R_\theta) = \bar{M}_w^{-1} P^{-1}(\theta) \quad (8)$$

As the reciprocal of the particle-scattering factor $P(\theta)$ is given by¹¹

$$P^{-1}(\theta) = 1 + u/3$$

where $u = 16\pi^2 n_1^2 \lambda^{-2} \langle S^2 \rangle \sin^2(\theta/2)$, then eqs. (7) and (8) on combination with eq. (6) give for the simultaneous variation of the experimental c/Q_θ with c and θ :

$$\begin{aligned} c/Q_\theta = (W/K^*)\bar{M}_w^{-1} [1 + (16/3)\pi^2 n_1^2 \lambda^{-2} \langle S^2 \rangle \sin^2(\theta/2)] \\ + (W/K^*)2A_2c + (W/K^*)3A_3c^2 \quad (9) \end{aligned}$$

Values of c/Q_θ are obtained from experimental figures by the first part of the program, which transforms them (Table I) via the subsequent simple operations indicated, to the final required form of Table II.

Then, for all the $2(1+L)(1+K)$ entries, evaluation is made of (1) $I = fG$; (2) I/I_0 , where I_0 is the intensity at $\theta = 0$; (3) $B_\theta = (I/I_0)_{\text{soln.}} - (I/I_0)_{\text{solv.}}$; and (4) $c/Q_\theta = c/[\sin \theta / (1 + \cos^2 \theta)][B_\theta - 2RB_{180-\theta}]$.

TABLE I

An- gles	Solvent		Concentrations						
			c_1		c_2		...	c_L	
	G_{solv}	f	G_1	f	G_2	f		G_L	f
0									
θ_1									
θ_2									
.									
.									
.									
θ_K									

TABLE II
LK Entries of c/Q_θ

	c_1	c_2	...	c_L
θ_1				
θ_2				
.				
.				
.				
θ_K				

LEAST SQUARES AND PROGRAMMED TREATMENT

Writing \bar{X}_{ij} for c/Q_θ at θ_i and c_j , we seek to fit a function X by least squares to \bar{X}_{ij} , thus

$$X = l + mx_i + nc_j + bc_j^2 \quad (10)$$

where $x_i = \sin^2(\theta/2)$, and the coefficients l , m , n , and b are to be determined to give best fit. It is necessary, therefore, to minimize

$$\begin{aligned}
 E &= \sum_{i=1}^K \sum_{j=1}^L (X_{ij} - \bar{X}_{ij})^2 \\
 &= \sum_{i=1}^K \sum_{j=1}^L \{ [(l + mx_i + nc_j + bc_j^2)]^2 - 2(l + mx_i + nc_j + bc_j^2)\bar{X}_{ij} \\
 &\quad + \bar{X}_{ij}^2 \}
 \end{aligned}$$

This is accomplished by solving

$$\partial E / \partial l = \partial E / \partial m = \partial E / \partial n = \partial E / \partial b = 0$$

These equations become, respectively:

$$\left. \begin{aligned}
 K Ll + \left(\sum_{i=1}^K x_i \right) L m + \left(\sum_{j=1}^L c_j \right) K n + \left(\sum_{j=1}^L c_j^2 \right) K b &= \sum_{i=1}^K \sum_{j=1}^L \bar{X}_{ij} \\
 \left(\sum_{i=1}^K x_i \right) L l + \left(\sum_{i=1}^K x_i^2 \right) L m + \left(\sum_{i=1}^K \sum_{j=1}^L x_i c_j \right) n & \\
 + \left(\sum_{i=1}^K \sum_{j=1}^L x_i c_j^2 \right) b &= \sum_{i=1}^K \sum_{j=1}^L x_i \bar{X}_{ij} \\
 \left(\sum_{j=1}^L c_j \right) K l + \left(\sum_{i=1}^K \sum_{j=1}^L x_i c_j \right) m + \left(\sum_{j=1}^L c_j^2 \right) K n + \left(\sum_{j=1}^L c_j^3 \right) K b & \\
 &= \sum_{i=1}^K \sum_{j=1}^L c_j \bar{X}_{ij} \\
 \left(\sum_{j=1}^L c_j^2 \right) K l + \left(\sum_{i=1}^K \sum_{j=1}^L x_i c_j^2 \right) m + \left(\sum_{j=1}^L c_j^3 \right) K n + \left(\sum_{j=1}^L c_j^4 \right) K b & \\
 &= \sum_{i=1}^K \sum_{j=1}^L c_j^2 \bar{X}_{ij}
 \end{aligned} \right\} \quad (11)$$

The second part of the program sets up the coefficients and right-hand sides of eq. (11) from the experimental data (c/Q_θ at different values of c and θ) manipulated in the first part. The equations are solved then by a standard ALGORITHM for l , m , n , and b the values of which are finally printed.

As a check on the fit, the third section of the program yields a table of the differences between experimental c/Q_θ values (Table II) and those given by the theoretical eq. (10) by using the derived values of l , m , n , and b . The table is printed for the concentrations and angles of the experiment.

CONVERSION OF COEFFICIENTS TO PARAMETERS OF SYSTEM

Comparison of eqs. (9) and (10) reveals that:

$$\left. \begin{aligned}
 l &= (W/K^*) \bar{M}_w^{-1}, \text{ whence } \bar{M}_w = (W/K^*)(1/l) \\
 m/l &= (16/3) \pi^2 n_1^2 \lambda^{-2} \langle S^2 \rangle, \text{ whence } \langle S^2 \rangle^{1/2} = 0.1378 (\lambda/n_1) (m/l)^{1/2} \\
 n &= (W/K^*) 2A_2, \text{ whence } A_2 = 0.5000 n (W/K^*)^{-1} \\
 b &= (W/K^*) 3A_3, \text{ whence } A_3 = 0.3333 b (W/K^*)^{-1}
 \end{aligned} \right\} \quad (12)$$

EXPERIMENTAL

Polymer

As the test material we have utilized the N.B.S. standard polystyrene sample 706 (U.S. National Bureau of Standards, Washington, D.C.) having the following certificated characteristics: \bar{M}_w by light scattering

= 257,800 as the mean of 12 determinations with a standard deviation of mean of 930; ratios of molecular weight $\bar{M}_z:\bar{M}_w:\bar{M}_n = 2.9:2.1:1.0$. Normally, of course, this would have served as an admirable standard for calibrating the instrument in terms of absolute turbidity. However, for our purpose \bar{M}_w was to be regarded as unknown and calibration effected via a theoretical value of R_{90} for pure toluene.

Procedure

Unpolarized light of $\lambda = 4358 \times 10^{-8}$ cm. was used. An initial solution ($c \approx 0.01$ g./ml.) in dry distilled toluene was filtered through two 1.5 μ Millipore bacteriological filters, subsequent dilutions with pure filtered solvent being made *in situ* in the small Witnauer cell, which was maintained at $30 \pm 0.1^\circ\text{C}$. by a heat exchanger already described elsewhere.¹² Measurements within the range $45\text{--}135^\circ$ were taken at intervals of 15° . While there is no practical objection to conducting readings below 45° , the instrument affords no facility for making them above 135° . As the corrected R_θ , eqs. (1) and (4) involves the intensity at $180^\circ - \theta$, the lowest usable angle is, consequently, 45° .

Value of W/K^* and Calibration

The factor W/K^* is required to determine the desired quantities from l , m , n , and b (as seen earlier it cancels out when determining $\langle S^2 \rangle^{1/2}$, which is given by the ratio m/l . Note that for the same reason the factor does not demand a knowledge of the refractive index of the solvent n_1 . The latter is needed solely for calculation of $\langle S^2 \rangle^{1/2}$). The factor is obtainable via eqs. (2) and (5) by using $TD = 0.306$, $R_w/R_c = 1.013$, $R = 0.039$ and $h = 1.20$ cm. We have utilized a value of 0.118 ml./g. for \bar{n} at 30°C . and $\lambda = 4358 \times 10^{-8}$ cm., which appears the most reliable of those available.¹³ Thus $W/K^* = 6.196 \times 10^5 [a(r/r')] \text{ g.}^2 \text{ cm.}^{-3} \text{ mole}^{-1}$. It is not recommended that the quoted value (0.040) for the working constant a be accepted definitively,⁹ and there are thus several approaches to evaluating $a(r/r')$, viz: (1) each of the two terms may be measured; (2) following Smart,¹⁰ the Rayleigh ratio of Perspex may be measured by using a polished solid block machined to the same dimensions as the small cylindrical cell; any subsequent readings of G_{90} and G_0 , coupled with this supposedly constant value, should yield the product $a(r/r')$ directly; (3) an alternative standard of well-accepted R_{90} may be incorporated.

Considering these approaches, the final one was adopted in view of the fact that a was found to be always greater than 0.040 and did in fact vary somewhat from experiment to experiment. Moreover, G_{90}/G_0 for the Perspex block decreased by about 25% over a period of 3 months. We have not investigated further the nature of any possible photochemical change occurring therein but have taken toluene as a calibration standard. Literature values¹⁴ of R_{90} for it (30°C . and $\lambda = 4358 \times 10^{-8}$ cm.) are in the range $(55.3\text{--}60.3) \times 10^{-6} \text{ cm.}^{-1}$ and hence we have selected the theoretical figure of $58.09 \times 10^{-6} \text{ cm.}^{-1}$ calculated from the Einstein-Cabannes equation.^{15,16} Some measure of support for this procedure is afforded by the work of Trossarelli and Saini¹⁷ and of Brewer.¹⁸ The former found that

Careful measurements led to good agreement with the theoretical R_{90} and the latter utilized such a value to arrive at an accurate molecular weight for a standard polystyrene sample. A multiplicative correction factor of (58.09/experimental R_{90}) has accordingly been introduced throughout. This ratio is generally of the order of 0.936–0.994. For the detailed example to be given, measured values of a , r/r' , and R_{90} -toluene are 0.0433, 1.475, and $58.47 \times 10^{-4} \text{ cm.}^{-1}$, respectively, whence W/K^* (corrected) = $6.196 \times 10^5(0.0433)(1.475)(58.09/58.47) = 3.932 \times 10^4 \text{ g.}^2 \text{ mole}^{-1}$. Subsequent reference to W/K^* will imply the corrected form.

RESULTS

Computer Output

The input data, together with $R = 0.039$ are assembled in the form of Table I. The values of θ for this example are 0, 45, 60, 75, 90, 105, 120, and 135°, and those of c are 0.010493, 0.006995, 0.003498, 0.001749, 0.0008744, and 0 g./ml. The corresponding derived values of c/Q_θ are printed in the form of Table II, should they be required. The results are shown in Table III, where concentrations proceed from left to right in the diminishing order quoted and angles proceed downwards in the increasing order stated. The first entry, for example, signifies that for $c = 0.010493$ g./ml. and $\theta = 45^\circ$, the value of c/Q_θ is 6.6159×10^{-1} , i.e., 0.66159.

TABLE III

6.6159 _{10⁻¹}	4.5258 _{10⁻¹}	2.9321 _{10⁻¹}	2.2270 _{10⁻¹}	1.9153 _{10⁻¹}
6.7068 _{10⁻¹}	4.6360 _{10⁻¹}	3.0132 _{10⁻¹}	2.3100 _{10⁻¹}	2.0296 _{10⁻¹}
6.7659 _{10⁻¹}	4.6994 _{10⁻¹}	3.0953 _{10⁻¹}	2.3883 _{10⁻¹}	2.1155 _{10⁻¹}
6.8877 _{10⁻¹}	4.8582 _{10⁻¹}	3.2386 _{10⁻¹}	2.5194 _{10⁻¹}	2.2497 _{10⁻¹}
6.8653 _{10⁻¹}	4.9144 _{10⁻¹}	3.3117 _{10⁻¹}	2.6326 _{10⁻¹}	2.3786 _{10⁻¹}
7.0007 _{10⁻¹}	5.0505 _{10⁻¹}	3.4283 _{10⁻¹}	2.7127 _{10⁻¹}	2.4553 _{10⁻¹}
7.0764 _{10⁻¹}	5.1563 _{10⁻¹}	3.5353 _{10⁻¹}	2.8148 _{10⁻¹}	2.5806 _{10⁻¹}

The required coefficients are printed thus:

$$\begin{aligned}
 l &= 1.5504_{10^{-1}} \\
 m/l &= 5.2562_{10^{-1}} \\
 n &= 3.0371_{10^{-1}} \\
 b &= 1.5443_{10^{-1}}
 \end{aligned}$$

The final check on the validity of these coefficients is printed and appears in Table IV, where the arrangement corresponds to that of Tables III and II.

In Table IV, the first entry, for example, denotes that the difference between the experimental c/Q_θ (= 0.66159) and that which obtains by reinserting the derived parameters into eq. (10) for the given c and θ is 5.9071×10^{-3} . This corresponds to a percentage difference of $100(0.0059071/0.66159) = +0.957\%$. Similarly, for the second entry in the first horizontal row, the percentage difference is $100(-0.0023949)/0.45258 = -0.529\%$. For all the entries the differences lie within the range of $\pm(0.04 \text{ to } 2.2)\%$, the majority being $< \pm 1\%$.

TABLE IV

5.9071 ₁₀ ⁻³	-2.3949 ₁₀ ⁻³	1.1062 ₁₀ ⁻³	-2.1165 ₁₀ ⁻³	-3.1822 ₁₀ ⁻³
6.5637 ₁₀ ⁻³	1.8961 ₁₀ ⁻⁴	7.8037 ₁₀ ⁻⁴	-2.2464 ₁₀ ⁻³	-1.9030 ₁₀ ⁻⁴
2.6469 ₁₀ ⁻³	-3.3008 ₁₀ ⁻³	-8.4339 ₁₀ ⁻⁴	-4.2513 ₁₀ ⁻³	-1.4191 ₁₀ ⁻³
4.2812 ₁₀ ⁻³	2.0348 ₁₀ ⁻³	2.9498 ₁₀ ⁻³	-1.6860 ₁₀ ⁻³	1.4556 ₁₀ ⁻³
-8.5098 ₁₀ ⁻³	-2.8897 ₁₀ ⁻³	-2.8716 ₁₀ ⁻⁴	-9.1108 ₁₀ ⁻⁴	3.7996 ₁₀ ⁻³
-4.7925 ₁₀ ⁻³	8.9192 ₁₀ ⁻⁴	1.5435 ₁₀ ⁻³	-2.7242 ₁₀ ⁻³	1.6429 ₁₀ ⁻³
-5.6586 ₁₀ ⁻³	3.0282 ₁₀ ⁻³	3.8027 ₁₀ ⁻³	-9.5396 ₁₀ ⁻⁴	5.7338 ₁₀ ⁻³

Derived Polymer and Polymer-Solvent Characteristics

Utilizing $n_1 = 1.5098$, $\lambda = 4358 \times 10^{-8}$ cm. and the previously given value of W/K^* , eqs. (12) together with the values of l , m , n , and b yield:

$$\begin{aligned}\bar{M}_w &= 2.54 \times 10^5 \\ \langle S^2 \rangle^{1/2} &= 288 \times 10^{-8} \\ A_2 &= 3.86 \times 10^{-4} \\ A_3 &= 1.31 \times 10^{-2}\end{aligned}$$

COMPARISON OF RESULTS WITH LITERATURE VALUES

The value of the molecular weight is seen to be ca. 1.5% less than that quoted by the N.B.S. The method has also yielded good precision, for the mean \bar{M}_w from several experiments is exactly 2.58×10^5 . It is rather more difficult to assess the accuracy of the remaining three quantities. For polystyrene of $\bar{M}_n = 2.48 \times 10^5$ (sharp fraction but no measure of polydispersity reported) in toluene at 25°C., Bawn et al.^{19,20} find $A_3 = 1.54 \times 10^{-2}$ from osmotic pressure measurements. No other directly comparable literature value appears to be available. In Tables V and VI are assembled some results (roughly within the required range of molecular weight), which have been published for A_2 and $\langle S^2 \rangle^{1/2}$, respectively. The solvent is toluene in all cases. Some of these values have been interpolated or calculated by us from the given data.

The value obtained for A_2 falls satisfactorily within the range of those quoted. From the relationship $A_3 = gA_2^2M$, a value of 0.34 may be derived for g , which is considered theoretically³⁵ to be $1/4$ or $5/8$. The root-mean-square radius of gyration is higher than the mean of the results in Table VI. The latter are, in the main, calculated figures from intrinsic viscosity and \bar{M}_w for example. The appropriate $\langle S^2 \rangle^{1/2}$ for them is therefore a weight-average, $\langle S^2 \rangle_w^{1/2}$, whereas our measured value and others in Table VI obtained by direct light-scattering measurements will be denoted by $\langle S^2 \rangle_{LS}^{1/2}$ (not necessarily Z-averages). In order to ascertain if there would be better accord between our experimental $\langle S^2 \rangle_{LS}^{1/2} = 288 \times 10^{-8}$ cm. and the other results we utilize the correlation factor due to Van Leemput and Stein,³⁶ viz.,

$$\langle S^2 \rangle_w^{1/2} = \langle S^2 \rangle_{LS}^{1/2} [(\gamma + 1)/(\gamma + 2 + \beta)]^{1/2}$$

TABLE V

$\bar{M}_w \times 10^{-5}$	Temp., °C.	$A_2 \times 10^4$ g. ⁻² cm. ³ mole	Reference
2.58 (isotactic)	30	3.60	21
1.92	30.3	3.28	22
3.92	30	3.3	23
2.82	25	1.0	24
4.90	Not quoted	3.3	25
3.57	20-30	3.8	26
2.95	25	4.05	27
2.58	25	3.35 ± 0.35	28

TABLE VI

$\bar{M}_w \times 10^{-5}$	Temp., °C.	$\langle S^2 \rangle^{1/2} \times 10^8$, cm.	Reference
3.92	30	244	23
2.58	30	207 ^a	23, 29
2.58	25	203 ^a	30
2.82	25	234	24
2.58	Not quoted	202 ^a	31
2.90	20	181	32
2.58	20	164 ^a	29, 32
2.58	25	197 ^a	22, 33
3.40	25	239 ^a	34
3.40	25	257 ^a	34

^a Calculated values.

in which (1) $\beta \approx (2\nu - 1)/2.43$, where ν is the Mark-Houwink exponent and (2) γ is the parameter characterizing the width of the distribution, thus $\bar{M}_w/\bar{M}_n = (\gamma + 1)/\gamma$. Fortunately it is known that $\bar{M}_w/\bar{M}_n = 2.1/1.0$ for the sample. Incorporating $\nu = 0.72$ it is seen that $\langle S^2 \rangle_w^{1/2} = 0.786 \times \langle S^2 \rangle_{LS}^{1/2}$. Hence, on a weight-average basis the root-mean-square radius of gyration becomes 226×10^{-8} cm., which, allowing for the somewhat lower temperature for the collected values in Table VI, yields better agreement.

CONCLUSIONS

The procedure is believed to be of utility not only by virtue of its convenience, but also because it obviates personal bias in fitting curves to experimental data. One example of this has already been indicated in the Introduction. While the ultimate accuracy of \bar{M}_w will be influenced by the independent measurement of \bar{n} , it may not be over-optimistic now in hoping for an improvement in the commonly accepted figure of $\pm 8\%$. For the accuracy attainable by light scattering. A particularly high value for a single entry in Table III may indicate a faulty measurement. In this case the relevant data could be omitted from the input and the remaining measurements utilized again on the computer. The appearance of dust in the solution may also be detected in this manner and the procedure amended similarly. However, if dilutions are made *in situ*, the high values

will persist throughout the table (in the order in which the measurements are made) after their first appearance. Unless the latter should happen to occur near the end of the table, no corrective procedure is available and all the data must be rejected. It has been stated already that c/Q_θ values are printed should they be required (which they will not, normally). The sole eventuality would be a confirmation of the points just mentioned via examination of irregularities in the Zimm plot.

Although our results cover low concentrations only, it is clear that deployment of the program to include a higher range of concentration should yield accurate third virial coefficients, values of which are currently lacking for most systems. In addition to their individual intrinsic importance they will also enable the following theoretically significant avenues to be investigated more easily: (1) interrelation of A_2 and A_3 , (2) dependence of A_2 and A_3 on molecular weight.

A further quantity obtainable directly from the results of one experiment is the expansion factor. Henley³⁷ has successfully utilized eq. (13) (based on the treatment of Orofino and Flory³⁸) to obtain the values of α for cellulose fractions in Cadoxen.

$$A_2 = (16\pi/3^{3/2})N_A(\bar{M}_w)^{-2}[\langle S^2 \rangle_{LS}^{1/2}]^3 \ln [1 + (\pi^{1/2}/2)(\alpha^2 - 1)] \quad (13)$$

In terms of the computer output this becomes

$$\alpha = \{1 + 1.13[(\text{antilog } \psi) - 1]\}^{1/2}$$

where

$$\psi = 1.42 \times 10^{-23}(\lambda/n_1)^{-3}(W/K^*)l^{-1/2}m^{-3/2}n$$

On evaluating ψ from the derived coefficients l , m , and n , the expansion coefficient α is found to be 1.48.

Finally, we should like to outline briefly how the program may be adapted to other situations. It is written in ALGOL for KDF9 and consequently uses the standard KDF9 procedures for input and output. The only changes necessary to run the program on another machine will be (1) alteration of the program heading; (2) alteration of \rightarrow at the end of the program; (3) elimination of *library* A0, A6, at the start of the program; (4) amendment of all calls of input/output procedures, i.e. open, close, read, format, write, write text, copy text. The exact significance of these parts of the program is explained elsewhere.³⁹

With regard to the light-scattering photometer, we recall that the first section of the tripartite program consists of a computation of c/Q_θ from experimental readings. Hence the program is specific to the Brice-Phoenix instrument, for the form assumed by R_θ , eqs. (1)–(4), is not the same as that obtained in other instruments. However, values of R_θ determined otherwise for other models, and thence c/R_θ (in place of our c/Q_θ), may be utilized directly as an input for the remaining two sections of the program. Conversion of the final l , m , n , and b to the required parameters will be accomplished simply in a similar but not identical fashion to that shown in eqs. (12).

APPENDIX

Computer Program

```

CBMM1JL00AP4→
begin library A0, A6;
real sz, szs, sc, scs, scf, scf, se, sce, sec, scse, R,
    wa, rad, xv, wc, wcs, ew;
integer K, Li, j, fone;
array a[1:4,1:4], x, b[1:4,1:1];
procedure ELIM (a, n, c, m, x); value a, n, c, m; real array a, c, x; integer m, n;
array a. n is the number of unknowns. The right-hand sides form a matrix stored in c where there are n rows and m columns. The values
the unknowns, on exit, are in the two-dimensional array x, with n rows and m columns, each column corresponding to the column in c;
integer i, j, k, p, q, t; real MAX, SUM, Q; integer array r[1:n];
for i: = 1 step 1 until n - 1 do
begin MAX: = 0;
for j: = 1 step 1 until n do
begin for p: = 1 step 1 until i-1 do if j = r[p] then goto L1;
if abs(MAX)-abs(a[j, i]) < 0 then
begin r[i] = j; MAX: = a[j, i] end;
L1: end;
q: = r[i];
for j: = 1 step 1 until n do
begin for p: = 1 step 1 until i do if j = r[p] then goto L4;
Q: = a[j, i]/MAX;
for k: = i + 1 step 1 until n do
a[j, k] = a[j, k] - Q × a[i, k];
for t: = 1 step 1 until m do c[j, t] = c[j, t] - Q × c[i, t];
L4: end
end;
end;

```

(continued)

```

SUM:= 0;
for p:= 1 step 1 until n-1 do SUM:= r[p] + SUM;
r[n]:= n × (n + 1) ÷ 2 - SUM;
for i:= n step -1 until 1 do
begin q:= r[i];
for t:= 1 step 1 until m do
begin SUM:= 0; if i = n then goto L3;
for j:= i + 1 step 1 until n do SUM:= x[j,i] × a[q,j] + SUM;
L3: x[i,i]:= (c[q,i] - SUM)/a[q,i];
end
end
end;
fone:= format (4s - d.ddddd10 + nd);
open (20); open (30); rad:= 3.14159265/180.0;
comment This section calculates C/Q theta;
start: copy text (20,30,[1])
R:= read (20); if R = 0 then goto finish;
K:= read (20); L:= read (20);
begin array I[1:K + 1,1:L + 1],B,X[1:K,1:L],C[1:L + 1],
theta[1:K + 1];
for i:= 1 step 1 until L + 1 do C[i]:= read (20);
for i:= 1 step 1 until K + 1 do
begin theta[i]:= read (20) × rad;
for j:= 1 step 1 until L + 1 do I[i,j]:= read (20) × read (20)
end;
for i:= 1 step 1 until K do
begin wa:= I[i + 1,L + 1]/I[1,L + 1];
for j:= 1 step 1 until L do B[i,j]:= I[i + 1,j]/I[1,j] - wa
end;
for i:= 1 step 1 until K do
begin wa:= sin (theta[i + 1])/(1.0 + cos(theta[i + 1] ↑ 2));
write text (30,[[c]]);
for j:= 1 step 1 until L do

```

(continued)

```

begin X[i,j] := C[j]/(B[i,j] - 2.0 × R × B[K + 1 - i,j])/wa;
write (30,ione,X[i,j]);
if j = j ÷ 5 × 5 then write text (30,[c1]);
end
end;
comment This section does the least squares fit;
sz := srs := sc := scs := scc := scf := se := sze := sce := scse := 0.0;
for j := 1 step 1 until L do
begin wc := C[j]; wcs := wc + wc;
sc := sc + wc; scs := scs + wcs;
scc := scc + wcs × wc; scf := scf + wcs × wcs
end;
for i := 1 step 1 until K do
begin xw := sin(theta[i + 1]/2.0); xw := xw × xw;
sx := sx + xw; sxs := sxs + xw × xw;
for j := 1 step 1 until L do
begin ew := X[i,j]; wc := C[j];
se := se + ew;
sxe := sxe + xw × ew;
sce := sce + wc × ew;
scse := scse + wc × wc ×
end
end;

```

(continued)

```

a[1,1]:= K X L; a[1,2]:= a[2,1]:= L X sx;
a[1,3]:= a[3,1]:= K X sc; a[1,4]:= a[4,1]:= K X scs;
a[2,2]:= L X sxs; a[2,3]:= a[3,2]:= sx X sc;
a[2,4]:= a[4,2]:= sx X scs;
a[3,3]:= K X scs; a[3,4]:= a[4,3]:= K X scs;
a[4,4]:= K X scf;
b[1,1]:= se; b[2,1]:= sre; b[3,1]:= sce; b[4,1]:= scse;
ELIM(a,4,b,1,x);
write text (30,[c]1 = 1); write (30,fone,x[1,1]);
write text (30,[c]m/1 = 1); write (30,fone,x[2,1]/x[1,1]);
write text (30,[c]n = 1); write (30,fone,x[3,1]);
write text (30,[c]b = 1); write (30,fone,x[4,1]);
write text (30,[p]1);
for i:= 1 step 1 until K do
begin xv:= sin(theta[i + 1]/2.0); xv:= xv X xv;
write text (30,[c]1);
for j:= 1 step 1 until L do
begin write (30,fone,X[i,j] - x[1,1] X xv - x[3,1] X C[j]
- x[4,1] X C[j] X C[j]);
if j = j + 5 X 5 then write text (30,[c]1);
end;
end;
end;
goto start;
finish: close (20); close (30);
end→

```

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Résumé

Un programme de calculateur ALGOL a été mis au point en vue de manipuler les résultats de diffusion de la lumière obtenus avec un photomètre de Brice-Phoenix. L'entrée consiste dans les valeurs expérimentales des déviations galvanométriques et les facteurs des filtres utilisés à chaque concentration c et angle de mesure θ . Ces valeurs sont transformées en variables appropriées dans l'équation fondamentale comprenant le facteur de diffusion de la particule, à savoir: $c/Q_\theta = (W/K^*)\bar{M}_w^{-1}[1 + (16/3)\pi^2 n_1^2 \lambda^2 \langle S^2 \rangle \sin^2(\theta/2)] + (W/K) \cdot 2A_2c + (W/K^*) \cdot 3A_3c^2$, dans laquelle Q_θ est une forme corrigée du rapport de Rayleigh et (W/K^*) est un terme constant composite pour l'instrument et le système polymère-solvant. Désignant \bar{X}_{ij} pour la variable c/Q_θ à θ_i et c_j , une fonction X peut être trouvée par les moindres carrés s'accorder avec \bar{X}_{ij} , donc $X = e + m \sin(\theta/2) + nc_j + bc_j^2$. Les équations provenant de la minimisation de $\sum_{i=1}^K (X_{ij} - \bar{X}_{ij})^2$ sont solutionnées par le calculateur pour fournir les coefficients correspondants le mieux pour e , m , n et b . Ceux-ci peuvent être reliés simplement au poids moléculaire, au rayon de gyration du carré moyen, au second et troisième coefficient viriel respectivement. La portion finale du programme est désignée pour rectifier l'accord de ces coefficients. Il fournit un tableau des différences entre toutes les valeurs expérimentales c/Q_θ et les valeurs correspondantes obtenues en insérant les dérivées e , m , n et b dans les équations fondamentales. Le procédé a été essayé de façon satisfaisante en utilisant un échantillon bien étalonné de polystyrène dans le toluène à 30°C à une longueur d'onde de 436 m μ .

Zusammenfassung

Ein ALGOL-Computerprogramm zur Behandlung der mit dem Brice-Phoenix-Photometer erhaltenen Lichtstreuungsdaten wurde aufgestellt. Die Eingabe besteht aus den experimentellen Galvanometerausschlägen und den für jede Konzentration c und jeden Messwinkel θ verwendeten Filterfaktoren. Diese werden in der den Teilchenstreuungsfaktor einschliessenden Fundamentalgleichung $c/Q_\theta = (W/K^*)\bar{M}_w^{-1}[1 + (16/3)\pi^2 n_1^2 \lambda^2 \langle S^2 \rangle \sin^2(\theta/2) + (W/K) \cdot 2A_2c + (W/K^*) \cdot 3A_3c^2$, wo Q_θ ein korrigierte Form des Rayleighverhältnisses und (W/K^*) ein zusammengesetzter konstanter Term für das Instrument und das Polymer-Lösungsmittelsystem ist, in die geeigneten Variablen umgewandelt. Schreibt man für die Variable c/Q_θ bei θ_i und c_j X_{ij} so ergibt sich nach der Methode der kleinsten Quadrate eine Funktion X zur Darstellung von \bar{X}_{ij} , nämlich $X = 1 + m \sin(\theta/2) + nc_j + bc_j^2$. Die aus der Aufsuchung des Minimums von $\sum_{i=1}^K (X_{ij} - \bar{X}_{ij})^2$ erhaltenen Gleichungen werden vom Computer unter Lieferung der besten Anpassungskoeffizienten l , m , n und b gelöst. Diese können in einfacher Weise zum Molekulargewicht, zur Wurzel aus dem mittleren Quadrat des Gyrationradius sowie zum zweiten und dritten Virialkoeffizienten in Beziehung gebracht werden. Der letzte Teil des Programmes dient zur Überprüfung der Anpassung dieser Koeffizienten. Er liefert eine Tabelle der Differenzen zwischen allen experimentellen c/Q_θ -Werten und den entsprechenden, durch Einsetzung der abgeleiteten Grössen l , m , n und b in die Fundamentalgleichung erhaltenen Werten. Das Verfahren wurde an einer gut standardisierten Polystyrolprobe in Toluol bei 30°C und einer Wellenlänge von 436 m μ mit befriedigendem Erfolg getestet.

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