

Stefan-Maxwell coefficients R_{ij} based on volume fraction driving force. The D_{ij} may be measured more accurately experimentally, but show greater concentration dependence than the R_{ij} . Neither set may generally be predicted from binary data. The molecular significance of neither set is known.

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Multicomponent Diffusion Involving High Polymers. II.

Characterization of Polydispersity from Diffusion Data

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Polydispersity may be described by average diffusion coefficients. This work develops the theory for the determination of these coefficients with the Gouy interferometer. If a particular form of the distribution function of diffusion coefficients is assumed, number-average and weight-average molecular weights may be calculated. Two polystyrenes of broad molecular weight distribution are studied in cyclohexane at 35°.

If a polymer sample is sufficiently dilute, the various species diffuse independently. In this case, diffusion data can be used to measure the polydispersity; that is, the distribution of the sizes of the polymer molecules. Usually, instead of actually measuring this distribution, average molecular weights are determined by osmotic pressure, light scattering, or ultracentrifuge measurements. In a similar fashion, Daune and Benoit¹ suggested measurement of the average diffusion coefficients D_1 and D_2

$$D_1 = \left[\int_0^\infty D^{-1/2} g(D) dD \right]^2 \quad (1)$$

$$D_2 = \frac{\int_0^\infty D^{-1/2} g(D) dD}{\int_0^\infty D^{-3/2} g(D) dD} \quad (2)$$

where D is the diffusion coefficient and $g(D)$ is the distribution of diffusion coefficients. Using a Jamin

interferometer, Daune, Benoit, and co-workers²⁻⁵ evaluated D_1 and D_2 for several systems. This paper develops the theory of measurement of average diffusion coefficients with the Gouy interferometer and presents results for two polystyrenes.

Theory. The Gouy interferometer measures the refractive index gradient for one-dimensional, isothermal diffusion.⁶ If the solution is sufficiently dilute, each polymer species diffuses independently. For a con-

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(1) M. Daune and H. Benoit, *J. chim. phys.*, **51**, 233 (1955).

(2) M. Daune, H. Benoit, and Ch. Sadron, *J. Polymer Sci.*, **16**, 483 (1955).

(3) M. Daune, H. Benoit, and G. Scheibling, *J. chim. phys.*, **54**, 924 (1957).

(4) R. N. Mukherjee and P. Rempp, *ibid.*, **56**, 94 (1959).

(5) R. Varoqui, M. Jacob, L. Freund, and M. Daune, *ibid.*, **59**, 161 (1962).

(6) L. J. Gosting, *Advan. Protein Chem.*, **11**, 476 (1956).

stant diffusion coefficient D and constant partial specific volumes, the concentration profile for free diffusion is

$$\frac{\rho - \rho_0}{\frac{\Delta \rho_0}{2}} = \operatorname{erf} \frac{x}{\sqrt{4Dt}} \quad (3)$$

where ρ is the mass concentration, ρ_0 the average mass concentration, $\Delta \rho$ the mass concentration difference, x the cell coordinate, and t the time. Except at the Θ -temperature, the assumption of constant D is poor.^{5,7,8} Experiments at temperatures other than the Θ -temperature must be repeated at different $\Delta \rho$ to ensure that the concentration dependence of the diffusion coefficient is not significant. The concentration dependence of the measured parameters may be removed by extrapolating *vs.* the concentration difference squared.^{9,10}

If each species varies linearly with refractive index, the refractive index profile is

$$\frac{n - n_0}{\left(\frac{\Delta n}{2}\right)} = \int_0^\infty \operatorname{erf} \frac{x}{\sqrt{4Dt}} g(D) dD \quad (4)$$

The refractive index gradient $\partial n / \partial x$ is

$$\frac{\partial n}{\partial x} = \frac{\Delta n}{2} \int_0^\infty \frac{e^{-x^2/4Dt}}{\sqrt{\pi Dt}} g(D) dD \quad (5)$$

with a maximum at $x = 0$

$$\left(\frac{\partial n}{\partial x}\right)_{\max} = \frac{\Delta n}{\sqrt{4\pi t}} \int_0^\infty g(D) D^{-1/2} dD \quad (6)$$

Combining eq. 6 with eq. 1

$$D_1 = \frac{(\Delta n)^2}{4\pi t (\partial n / \partial x)_{\max}^2} \quad (7)$$

D_1 is identical with the "reduced height-area ratio" \mathfrak{D}_A ,¹¹ which is measured by the Gouy method.

The second average diffusion coefficient D_2 is found from the deviation of the refractive index gradient given in eq. 5 from Gaussian shape. We define an "idealized cell coordinate" ζ as the value of $x/\sqrt{4Dt}$ for a particular fringe if the polymer were monodisperse. This parameter ζ is a function only of the Gouy fringe number j . Next, we define the "fringe deviation" Ω as¹²

$$\Omega = e^{-\zeta^2} - \frac{(\partial n / \partial x)}{(\partial n / \partial x)_{\max}} \quad (8)$$

Combining eq. 5, 7, and 8 gives

$$\Omega = e^{-\zeta^2} - \int_0^\infty g(D) \sqrt{\frac{D_1}{D}} e^{-x^2/4Dt} dD \quad (9)$$

If we find x as a function of ζ , we may expand eq. 9 as a power series in ζ to obtain an expression for D_2 . This derivation is given in the Appendix. The result is

$$\Omega = \frac{1}{3} \left[\left(\frac{D_1}{D_2} \right) - 1 \right] \zeta^2 + 0(\zeta^4) \quad (10)$$

This equation allows determination of the second average diffusion coefficient.^{13,14}

Unfortunately, the two average diffusion coefficients defined above do not have the same physical significance as the number-average and weight-average molecular weights. The ratio of these average molecular weights is often the desired result. To obtain them, Daune and Benoit postulated a two-parameter form of the distribution function

$$g(D) = \frac{1}{D_0} \frac{\beta^\beta}{\Gamma(\beta)} \left(\frac{D_0}{D} \right)^{\beta+2} e^{-\beta(D_0/D)} \quad (11)$$

The parameters D_0 and β may be found from D_1 and D_2 . The average molecular weights are found using the relation

$$f(M) dM = g(D) dD \quad (12)$$

where $f(M)$ is the distribution of molecular weights.

To determine how well the assumed distribution function fits the data, we require another experimental parameter, the area under the fringe deviation graph Q

$$Q = \int_0^1 \Omega df(j) \quad (13)$$

where $f(j)$ is the interference condition discussed in detail in the Appendix. The parameter Q is used in the analysis of coupled ternary diffusion problems¹⁵ and has proved the most successful method of analyzing the deviations of the refractive index profile from Gaussian shape.

(7) S. I. Klenine, H. Benoit, and M. Daune, *Compt. rend.*, **250**, 3174 (1960).

(8) V. N. Tsvetkov and S. I. Klenine, *J. Polymer Sci.*, **30**, 187 (1958).

(9) L. J. Gosting and H. Fujita, *J. Am. Chem. Soc.*, **79**, 1359 (1957).

(10) E. L. Cussler, Jr., and E. N. Lightfoot, *J. Phys. Chem.*, **69**, 1135 (1965).

(11) P. J. Dunlop and L. J. Gosting, *J. Am. Chem. Soc.*, **77**, 5238 (1955).

(12) D. A. Akeley and L. J. Gosting, *ibid.*, **75**, 5685 (1953).

(13) The reduced second moment and the reduced fourth moment defined for the Gouy theory do not give useful average diffusion coefficients.

(14) R. L. Baldwin, P. J. Dunlop, and L. J. Gosting, *J. Am. Chem. Soc.*, **77**, 5235 (1955).

(15) H. Fujita and L. J. Gosting, *J. Phys. Chem.*, **64**, 1256 (1960).

To evaluate Q in terms of the distribution functions, we combine eq. 8 and 13 to obtain

$$Q = \int_0^\infty e^{-\zeta^2} \frac{\partial f(j)}{\partial \zeta} d\zeta - \int_0^\infty \frac{\partial n/\partial x}{(\partial n/\partial x)_{\max}} \frac{\partial f(j)}{\partial y} dy \quad (14)$$

where $y = x\sqrt{4D_A t}$. These derivatives may be found by differentiating eq. 23 and 25 in the Appendix. The results are

$$\frac{\partial f(j)}{\partial \zeta} = \frac{4}{\sqrt{\pi}} \zeta^2 e^{-\zeta^2} \quad (15)$$

$$\frac{\partial f(j)}{\partial y} = \frac{4}{\sqrt{\pi}} \int_0^\infty g(D) y^2 \delta^3 e^{-y^2 \delta^2} dD \quad (16)$$

where $\delta = (D_A/D)^{1/2}$. By inserting these derivatives into eq. 14, subscripting the two different integration variables previously called D , and integrating over ζ and y , we obtain

$$Q = 2^{-3/2} - \int_0^\infty \int_0^\infty g(D_i) g(D_j) \frac{(D_i/D_t)^{1/2}}{(D_j/D_t + 1)^{3/2}} dD_i dD_j \quad (17)$$

If the species is monodisperse, $g(D)$ becomes the Dirac δ function and Q is zero.

For the form of $g(D)$ given in eq. 11, we have

$$Q = 2^{-3/2} - \left(\frac{D_0}{D_t}\right)^{1/2} \int_0^\infty \int_0^\infty \frac{\left(\frac{D_0}{D_i}\right)^{\beta+1/2} \left(\frac{D_0}{D_j}\right)^{\beta+3/2}}{\left(\frac{D_0}{D_i} + \frac{D_0}{D_j}\right)^{\beta+3/2}} \times \exp\left[-\beta\left(\frac{D_0}{D_i} + \frac{D_0}{D_j}\right)\right] d\left(\frac{D_0}{D_i}\right) d\left(\frac{D_0}{D_j}\right) \quad (18)$$

Using the variable substitutions

$$\frac{D_0}{D_i} = r \cos \theta; \quad \frac{D_0}{D_j} = r \sin \theta \quad (19)$$

the above equation may be directly integrated

$$Q = 2^{-3/2} - \frac{\Gamma(2\beta + 5/2)\Gamma(\beta + 5/2)}{\Gamma(2\beta + 4)\Gamma(\beta + 1)} \quad (20)$$

Thus, a measurement of Q provides a check on the parameter β .

From an experiment with the Gouy interferometer, we find the two average diffusion coefficients D_1 and D_2 . From these two true averages, we may determine values for D_0 and β of the assumed distribution. At the same time, we can obtain a value of β from Q which is based on the assumption that the polymer

does fit this type of distribution. Comparison of the values of β obtained in these two ways shows how well the sample fits the assumed distribution. If we decide that, for our purposes, this assumption is satisfied, we may use our knowledge of $g(D)$ to calculate M_n and M_w .

Experimental

Materials and Solutions. Two polystyrene samples were studied. The first was National Bureau of Standards standard sample No. 706, a polystyrene of broad molecular weight distribution. The number-average molecular weight by osmotic pressure measurements with No. 600 cellophane membranes was 136,500. This value should be the upper limit of the true value. The National Bureau of Standards reported weight-average molecular weights of 257,800 (measured by light scattering) and 288,100 (measured by sedimentation equilibrium). A value for the weight-average molecular weight of 278,000 was obtained from sedimentation equilibrium by Osterhaut.¹⁶ The sample used in these experiments was provided by Dr. Osterhaut.

The second polymer sample, designated 19F, was provided by Professor J. D. Ferry of the Department of Chemistry at the University of Wisconsin. It was originally supplied by Dr. R. F. Boyer of the Dow Chemical Co. as a preparation having substantially the most probable molecular weight distribution. It had a number-average molecular weight of 197,000 by osmotic measurements,¹⁷ and a weight-average molecular weight of 370,000 by light scattering measurements¹⁸ and of 375,000 by sedimentation velocity experiments.¹⁹ However, a value of 456,000 has been reported for sedimentation equilibrium experiments.¹⁶ Both polymers were studied in reagent grade cyclohexane at 35°.

Apparatus. The Gouy interferometer^{6,11,12,20-22} used in these experiments has been fully described elsewhere. The temperature was measured to $\pm 0.002^\circ$ with a mercury-in-glass thermometer calibrated against a standard thermometer belonging to Professor J. W. Williams. It was found to read 34.966° at a true

(16) H. W. Osterhaut, Ph.D. Thesis, University of Wisconsin, 1964.

(17) L. E. Grandine, Jr., Ph.D. Thesis, University of Wisconsin, 1952.

(18) D. J. Streeter and R. F. Boyer, *Ind. Eng. Chem.*, **43**, 1790 (1951).

(19) J. F. Blair and J. W. Williams, *J. Phys. Chem.*, **68**, 161 (1964).

(20) L. J. Gosting, E. M. Hanson, G. Kegeles, and M. S. Morris, *Rev. Sci. Instr.*, **20**, 209 (1949).

(21) L. A. Woolf, D. G. Miller, and L. J. Gosting, *J. Am. Chem. Soc.*, **84**, 317 (1962).

(22) R. L. Rettig, Ph.D. Thesis, University of Wisconsin, 1964.

Table I: Polystyrene in Cyclohexane at 35°

Expt. no.	Polymer	Average mass fraction	Mass fraction difference	$T, ^\circ\text{C.}$	J	$D_1 \times 10^7$	$D_2 \times 10^7$	$Q \times 10^4$	β from D_1/D_2	β from Q	β from M_w/M_n
47	NBS 706	0.00721	0.01442	35.003 ± 0.004	86.483	2.578	2.124	169.6	2.70	2.80	2.38
48	19F	0.00629	0.01259	35.014 ± 0.002	76.019	2.070	1.676	191.3	2.38	2.36	2.38

35.000°. A 110-volt constant input heater equipped with a Variac was used to supplement the usual temperature control. All calculations were made on an IBM 1620 computer belonging to the Wisconsin College of Engineering.

Results

The experimental results for polymers NBS 706 and 19F are given in Table I. In this table, D_1 and D_2 are reported separately, although it is D_1 and D_1/D_2 which are found experimentally. These values are used to determine a value of β from eq. 1, 2, and 10. The value of β for Q is found from eq. 20. For comparison with these values, a value of β has been calculated from M_w/M_n by assuming $D = kM^{-0.5}$. The value of 0.5 is given by the theory of a flexible chain polymer in a poor solvent. Experimental values of the exponent range from 0.48 to 0.51.^{23,24} The ratio of M_w/M_n was based on light scattering data and osmotic pressure data for the calculations. Thus, values of β obtained from D_1/D_2 , from Q , and from M_w/M_n can be compared.

Discussion

The average diffusion coefficients D_1 and D_2 reported above are reproducible within 0.5%. As such, they are an accurate, reproducible method of analyzing polydispersity. Their chief disadvantage is that they are not in common use. The assumption of a particular form of distribution function $g(D)$ which is necessary to convert the diffusion data into molecular weight data prevents the calculation of the accurate molecular weights which are commonly reported. This is shown by both polydisperse polymers which were studied.

For polymer NBS 706, the values obtained for β from D_1/D_2 and Q differ by about 4%, indicating that the Shultz distribution is not a good assumption for this polymer. This is in agreement with results obtained on this polymer from sedimentation equilibrium.¹⁴ Sedimentation equilibrium measures M_w , M_z , and M_{z+1} and fits these parameters to a Shultz-type distribution. Thus, the procedure weights the larger molecules more heavily. It gives $M_w/M_n = 1.67$. The Gouy technique reported in this paper

weights the smaller molecules more heavily. Using the value of $\beta = 2.70$, $M_w/M_n = 2.18$. These values bracket the directly measured value of 1.887.

For polymer 19F, the values obtained for β by the two methods differ by less than 1%, indicating that the actual distribution function is nearly the assumed form. Thus, the value of β found from M_w/M_n should be nearly the same. It is. However, since there is disagreement about the actual value of M_w/M_n for this polymer,¹⁶ this close agreement must be viewed with some skepticism.

The success of this technique depends on the goal of the experimentalist. If he is interested in the molecular weight distribution of the polymer as a goal in itself, then he should use the established methods of fractionation or of the ultracentrifuge. If his goal is the measurement of some other physical property, such as viscosity or chemical potential, then he can use the technique of average diffusion coefficients. If a Θ -solvent is known, one experiment is sufficient; if not, at least two are required. The result is an accurately known ratio D_1/D_2 characterizing polydispersity. From this ratio, M_w/M_n may be calculated. The diffusion data provide an internal check on the probable success of this calculation in the comparison of the distribution found from the average diffusion coefficient ratio D_1/D_2 and that found from the area under the fringe deviation graph Q . This check and the accuracy with which D_1/D_2 is known are the strengths of this technique.

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Appendix

The interference condition derived from wave optics for the Gouy interferometer is²⁵

(23) H. W. McCormick, *J. Polymer Sci.*, **36**, 341 (1959).

(24) H. J. Cantow, *Macromol. Chem.*, **30**, 169 (1959).

$$f(j) = \frac{j + 3/4 + C}{J} \quad (21)$$

where J is the total number of fringes; j is the fringe number, measured from the bottom of the pattern; and C is a small wave optical correction factor. In terms of the refractive index, this is

$$f(j) = \frac{2}{\Delta n} \left[(n - n_0) - x \frac{\partial n}{\partial x} \right] \quad (22)$$

which for our system is combined with eq. 4 and 5 to give

$$f(j) = \int_0^\infty g(D) \left[\operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) - \frac{x^2}{\sqrt{\pi Dt}} e^{-x^2/4Dt} \right] dD \quad (23)$$

We next define an "idealized cell coordinate" ζ by

$$\frac{n - n_0}{\Delta n/2} = \operatorname{erf} \zeta \quad (24)$$

If the system were monodisperse, then $\zeta = x/\sqrt{4Dt}$. In terms of ζ , the interference condition is

$$f(j) = \operatorname{erf} \zeta - \frac{2}{\sqrt{\pi}} \zeta e^{-\zeta^2} \quad (25)$$

We want to find Ω (cf. eq. 10) as a power series in ζ . In principle, this is simple. We want to combine eq. 23 and 25 and solve for x in terms of ζ . Then we want to insert this result into eq. 5 to find dn/dx in terms of ζ and then combine with eq. 8 to give the desired equation. In practice, this is difficult.

First we define the new variables y and δ

$$y = \frac{x}{\sqrt{4D_A t}} \quad \delta = \sqrt{\frac{D_A}{D}} \quad (26)$$

Then we define a generalized interference condition of the arbitrary variable, ξ

$$f(\xi) = \operatorname{erf} \xi - \frac{2}{\sqrt{\pi}} \xi e^{-\xi^2} \quad (27)$$

For example

$$f(\zeta) = \int_0^\infty g(D) f(y\delta) dD \quad (28)$$

If we define a deviation variable σ by the relation

$$\sigma = f(y) - f(\zeta) \quad (29)$$

then

$$\sigma = \int_0^\infty g(D) [f(y) - f(y\delta)] dD \quad (30)$$

Expanding this as a Taylor series, we may write

$$\sigma = \sum_{l=0}^{\infty} \frac{\sigma^l}{l!} \frac{\partial^l}{\partial f(\zeta)^l} \left[\int_0^\infty g(D) (f(\zeta) - f(\delta\zeta)) dD \right] \quad (31)$$

Neglecting all but the first two terms and solving for σ gives

$$\sigma = \frac{\int_0^\infty g(D) (f(\zeta) - f(\delta\zeta)) dD}{\int_0^\infty g(D) \delta^2 e^{-\zeta^2(\delta^2 - 1)} dD} \quad (32)$$

Now, from eq. 5 and 6, we expand $(\partial n/\partial x)/(\partial n/\partial x)_{\max}$ as a Taylor series in σ

$$\frac{(\partial n/\partial x)}{(\partial n/\partial x)_{\max}} = \sum_{m=0}^{\infty} \frac{\sigma^m}{m!} \frac{\partial^m}{\partial f(\zeta)^m} \left[\int_0^\infty g(D) \delta e^{-\zeta^2 \delta^2} dD \right] \quad (33)$$

Neglecting all but the first two terms and substituting eq. 32 for σ gives

$$\frac{(\partial n/\partial x)}{(\partial n/\partial x)_{\max}} = \int_0^\infty g(D) \delta e^{-\zeta^2 \delta^2} dD - \frac{\sqrt{\pi}}{2\zeta} \left[\int_0^\infty g(D) (f(\zeta) - f(\delta\zeta)) dD \right] \quad (34)$$

Substituting this into the definition of Ω (eq. 8) and expanding for small values of Ω gives

$$\Omega = 1/3 \left[\int_0^\infty g(D) \delta^3 dD - 1 \right] \zeta^2 + O(\zeta^4) \quad (35)$$

which is identical with eq. 10. This equation gives a method of determining D_1/D_2 for the Gouy interferometer.

(25) L. J. Gosting and L. Onsager, *J. Am. Chem. Soc.*, **74**, 6066 (1952).