bumin in 1% solution at *p*H 5 is increased from 0.045 to only 0.075 in 4 *M* urea, while the number of reacted disulfide groups increases from zero (reaction time of 24 hr.) to 5 in 4 *M* urea. This was after a reaction period of 10 minutes and the equilibrium value is undoubtedly considerably greater. It seems reasonable to conclude that unfolding or swelling, even to a slight extent as revealed by the slight increase of the viscosity, makes disulfide groups between helices much more reactive toward sulfite than they are in the native state.

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Lignin. X. Moment Relationship Derivation for the Distribution of Diffusion Coefficients in Polymers

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A derivation is given of an equation by which the distribution of diffusion coefficients can be evaluated in certain cases from concentration–position observations taken after a known time of diffusion of a polymer solute under "semi-infinite solid" geometry conditions.

Introduction

In the course of our studies of the distribution in molecular weights of lignin preparations,[2] it became desirable to be able to ascertain, at least approximately, the distribution of molecular weights or of diffusion coefficients within a separated polymer fraction. This can be done by repeated refractionations,[2b,3] but such procedures are tedious to carry out and they leave unresolved the question of what is the distribution in a particular fraction as finally obtained.

In certain cases the desired distribution can be estimated directly from diffusion data as previously recognized by Gralén[4] and by Daune and Freund.[5] In this Laboratory a solution-to-gel diffusion procedure[6] involving "semi-infinite solid" geometry[7] has been used to obtain estimates of mean diffusion coefficients. The data obtained in the course of carrying out this procedure, comprising measurements of solute concentrations at several distances from the boundary after a known time of diffusion, also can be used to obtain estimates of distribution of diffusion coefficients.

In Fig. 1A, the concentration–position data obtained from our diffusion experiments with vanillin and with a lignin sulfonate preparation are represented on a linear scale. In Fig. 1B, the same data are shown but with a "probability scale" for the ordinate, and it can be seen that a straight line is now obtained with the pure substance, vanillin. However, a curved line still is produced with the lignin sulfonate preparation and this curvature reflects the polydisperse nature of the preparation. The purpose of this paper is to set forth the derivation of an equation by which the statistical moments of the distribution of diffusion coefficients in polymers can be evaluated from data such as are illustrated in Fig. 1.

Moment Relationships

In general, the moment of integer order n, about a point b, for a continuous variable x, is defined[8-12] as

$$\alpha_n = \int_{-\infty}^{+\infty} (x - b)^n f(x) \, dx \tag{1a}$$

where $f(x)$ satisfies the condition

$$\int_{-\infty}^{+\infty} f(x) \, dx = 1$$

For a discrete variable, x_k, the moment is

$$\alpha_n = \sum_k (x_k - b)^n f(x_k) \tag{1b}$$

where $f(x_k)$ satisfies the condition

$$\sum_k f(x_k) = 1$$

When b is zero, equation 1 provides the "nth moment about the origin," μ'_n, and when b is the mean, there results the "nth moment about the mean," μ_n. A particular curve can thus yield any number of moments and in general a curve can be described in terms of an appropriate number of moments.[10]

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(1) Extracted from a Dissertation submitted by Jovan Moacanin in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Washington in 1956.

(2) (a) J. Moacanin, V. F. Felicetta, W. Haller and J. L. McCarthy, THIS JOURNAL, **77**, 3470 (1955); (b) V. F. Felicetta, A. Ahola and J. L. McCarthy, *ibid.*, **78**, 1899 (1956); (c) E. Nokihara, M. Jean Tuttle, V. F. Felicetta and J. L. McCarthy, *ibid.*, **79**, 4495 (1957); and (d) V. F. Felicetta and J. L. McCarthy, *ibid.*, **79**, 4499 (1957).

(3) P. Flory, "Chemistry of High Polymers," Cornell University Press, Ithaca, N. Y., 1953.

(4) N. Gralén, *Kolloid-Z.*, **95**, 188 (1941).

(5) M. Daune and L. Freund, *J. Poly. Sci.*, **23**, 115 (1957).

(6) V. F. Felicetta, A. E. Markham, Q. P. Peniston and J. L. McCarthy, THIS JOURNAL, **71**, 2879 (1949).

(7) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Clarendon Press, London, 1947.

(8) A. C. Aitken, "Statistical Mathematics," 7th Ed., Oliver and Boyd, London, 1952.

(9) R. von Mises, "Mathematical Theory of Probability and Statistics," Special Pub. 1, Grad. School of Engineering, Harvard Univ., 1946.

(10) M. G. Kendall, "Advanced Theory of Statistics," Vol. I, 3rd Ed., C. H. Griffin and Co., Ltd., London, 1947.

(11) W. Feller, "Introduction to Probability Theory and its Applications," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950.

The first moment about the origin is the mean value or mathematical expectation and the second moment about the mean is the variance or square of the standard deviation. Referring to the weight distribution of diffusion coefficients or, more conveniently, to the weight distribution of the square root of diffusion coefficients, the mean and the variance are

$$\mu'_{\mathrm{D}_1} = \sum_i (D_i^{1/2})\, w_i \qquad (2)$$

$$\mu_{\mathrm{D}_2} = \sum_i (D_i^{1/2} - \mu'_{\mathrm{D}_1})^2 w_i \qquad (3)$$

where w_i is the weight fraction of the ith component. It is desired to evaluate these and higher moments characteristic of the distribution of diffusion coefficients, *i.e.*, the "diffusivity moments" from experimental information such as that given in Fig. 1.

However, each curve of Fig. 1 has its own set of moments which here will be called "concentration moments" to distinguish them from the "diffusivity moments" mentioned above. The concentration moments about the origin readily can be evaluated graphically or otherwise directly from the experimental data of Fig. 1 by integrating expressions of the type

$$\mu'_{\mathrm{c}n} = \int_0^{+\infty} (x^n)\left(\frac{C_x}{C_0}\right) \mathrm{d}x \qquad (4)$$

where $n = 1, 2, 3 =$ positive integer. The number of moments significant to evaluate is limited only by the reliability of the data and the data processing.[12] It is now desired to establish a relationship between these concentration distribution moments and the diffusion distribution moments.

When a pure substance, or the ith component of a polymer system, diffuses according to Fick's law in one direction only, with constant diffusion coefficient D_i without interaction with other components and from a solution at substantially constant concentration, C_0, into a gel as described elsewhere,[6,12] then by integration of Fick's law it is found that after a diffusion time t, the concentrations C_x at various distances x from the boundary, are

$$\frac{C_{xi}}{C_{oi}} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\beta} e^{-y^2}\, \mathrm{d}y = 1 - \mathrm{erf}\, \beta = \mathrm{erfc}\, \beta \qquad (5)$$

where $\beta = x/\sigma_i$ and $\sigma_i = \sqrt{4D_it}$. When all components of a polymeric system diffuse simultaneously in this manner, the total concentration relationship is found by taking the sum over all components in the system as

$$\frac{C_x}{C_0} = \sum_i w_i \left(\frac{C_{x_i}}{C_{0i}}\right) = \sum_i w_i\, \mathrm{erfc}\, \beta \qquad (6)$$

and thus an equation of this type should provide an approximate fit for the experimental data represented in Fig. 1.

To relate equation 6 to the diffusivity moments, multiply both sides by the term x^{n-1} and then integrate between the limits zero and infinity to obtain the integral now designated as I

$$I = \int_0^{\infty} (x^{n-1})\left(\frac{C_x}{C_0}\right) \mathrm{d}x = \int_0^{\infty} \sum_i w_i\, (x^{n-1})\left[1 - \frac{3}{\sqrt{\pi}} \int_0^{\beta} e^{-y^2}\, \mathrm{d}y\right] \mathrm{d}x \qquad (7)$$

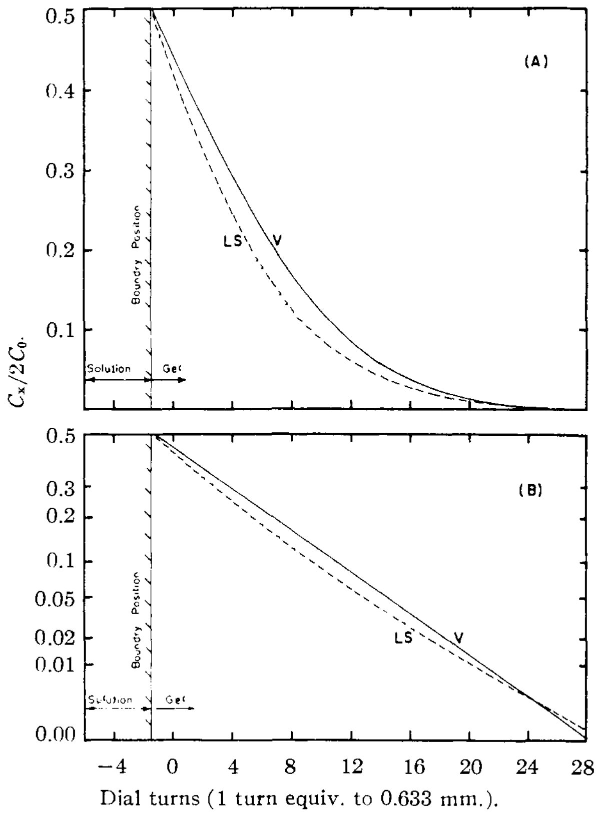

Fig. 1.—Concentration ratio on linear and probability scale *versus* distance into diffusion cell for vanillin and a polymeric lignin sulfonate preparation.

Since

$$x^{n-1} = (\beta\sigma_i)^{n-1} \text{ and } \mathrm{d}x = \sigma_i\, \mathrm{d}\beta \qquad (8)$$

then

$$I = \int_0^{\infty} \sum_i (w_i)(\sigma_i)^{n-1}(\beta)^{n-1}\left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\beta} e^{-y^2}\, \mathrm{d}y\right] \sigma_i\, \mathrm{d}\beta \qquad (9)$$

or

$$I = \sum_i w_i\sigma_i^n \int_0^{\infty} \beta^{n-1}\, \mathrm{erfc}\beta \mathrm{d}\beta = \sum_i \frac{w_i\sigma_i^n}{n} \int_0^{\infty} \mathrm{erfc}\, \beta \mathrm{d}(\beta^n) \qquad (10)$$

Designating the integral in the right-hand term of equation 10 by G, and integrating by parts

$$G = (\mathrm{erfc}\beta)\beta^n \Big|_{\beta = 0}^{\beta = \infty} - \int_0^{\infty} \beta^n\, \mathrm{d}(\mathrm{erfc}\, \beta) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \beta^n\, e^{-\beta^2}\, \mathrm{d}\beta \qquad (11a)$$

The right-hand side of equation 11 can be written as

$$G = \frac{1}{\sqrt{\pi}} \int_0^{\infty} [\beta^2]^{\left(\frac{n+1}{2} - 1\right)} [e]^{-\beta^2}\, \mathrm{d}(\beta^2) \qquad (11b)$$

and the integral is seen to be the gamma function of $(n + 1)(^1/_2)$ so that

$$G = \frac{1}{\sqrt{\pi}} \Gamma\left(\frac{n+1}{2}\right) \qquad (12a)$$

From known properties[13] of gamma functions (13, pages 93–98)

$$G = \frac{1}{\sqrt{\pi}} \left(\frac{n-1}{2}\right)! \qquad (12b)$$

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[12] J. Moacanin, H. Nelson, E. Back, V. F. Felicetta and J. L. McCarthy, THIS JOURNAL, **81**, 2051 (1959).

[13] M. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Company, New York, N. Y., 1956.

when n is an odd integer and

$$G = \frac{(n-1)}{(2)}\frac{(n-3)}{(2)}\cdots\cdots\frac{(1)}{(2)} \tag{12c}$$

when n is an even integer. Thus I can now be evaluated, and, since $\sigma_i = \sqrt{4D_it}$, one obtains

$$I = \frac{2^nt^{n/2}G}{n}\sum_i w_i\,(D_i{}^{1/2})^n \tag{13}$$

Substitution for I from equation 7 and rearrangement gives

$$\sum_i w_i\,(D_i{}^{1/2})^n = \frac{n}{2^nt^{n/2}G}\int_0^\infty x^{n-1}\left(\frac{C_x}{C_0}\right)\mathrm{d}x \tag{14}$$

The left-hand side of equation 14 is recognized as the expression for the nth moment of the distribution of $D^{1/2}$ about the origin

$$\mu'_{D_n} = \sum_i (w_i)(D_i{}^{1/2})^n \tag{15}$$

while the integral on the right-hand side of the equation is the $(n-1)$th moment of the distribution of concentration, C_x/C_0, about the origin

$$\mu'_{c\,n-1} = \int_0^\infty x^{n-1}\left(\frac{C_x}{C_0}\right)\mathrm{d}x \tag{16}$$

Thus equation 14 can be written in terms of the two types of moments as

$$\mu'_{D_n} = \frac{n}{2^nt^{n/2}G}\,\mu'_{c\,n-1} \tag{17}$$

and this is the desired general moment relationship. The specific equations for the first four moments of the distribution of $D^{1/2}$ about the origin follow from equation 17 with equations 12b and 12c

$$\mu'_{D_1} = \sum_i w_iD_i{}^{1/2} = \frac{\sqrt{\pi}}{2t^{1/2}}\int_0^{+\infty}\left(\frac{C_x}{C_0}\right)\mathrm{d}x = \left(\frac{0.886}{t^{1/2}}\right)\mu'_{c0} \tag{18}$$

$$\mu'_{D_2} = \sum_i w_iD_i = \frac{1}{t}\int_0^{+\infty}\left(\frac{C_x}{C_0}\right)x\mathrm{d}x = \left(\frac{1}{t}\right)\mu'_{c1} \tag{19}$$

$$\mu'_{D_3} = \sum_i w_iD_i{}^{3/2} = \left(\frac{3}{8}\right)\frac{\sqrt{\pi}}{t^{3/2}}\int_0^{+\infty}\left(\frac{C_x}{C_0}\right)x^2\mathrm{d}x = \left(\frac{0.665}{t^{3/2}}\right)\mu'_{c2} \tag{20}$$

$$\mu'_{D_4} = \sum_i w_iD_i{}^2 = \frac{1}{3t^2}\int_0^{+\infty}\left(\frac{C_x}{C_0}\right)x^3\mathrm{d}x = \left(\frac{1}{3t^2}\right)\mu'_{c3} \tag{21}$$

Numerical values of moments reflecting the distribution of diffusion coefficients of molecules comprising a polymeric system thus can be obtained from moments of the experimentally-obtained concentration–distribution curve. The degree of reliability with which we find this can be done under certain conditions is being reported in another communication.[12]

However, it is clear that, in practice, estimates of only the first few moments are available with an acceptable degree of accuracy so it is of interest to know how well these can be used to describe a distribution function. Several studies on this question have not led to a simple answer.[9] It has been reported that if two distributions have the same moments up to the order n, then graphs of the corresponding cumulative distribution functions must have at least n intersections.[9] Thus it seems justified to conclude that two monotonic curves with a large number of intersections cannot in general be far distant from each other. If it is assumed that the probability functions for diffusion coefficients or for molecular weights of polymer molecules have no discontinuities and also are unimodal, it then appears improbable that two distributions with identical first few moments will differ greatly. The authors appreciate Mr. D. A. Ratkowsky's suggestions concerning this paper.

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Lignin. XI. Estimation of Polymolecularity in Lignin Sulfonate Polymers from Diffusion Measurements

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From concentration-position observations taken after a known time of diffusion of a polymer solute under "semi-infinite solid" geometry conditions, the statistical moments of the distribution in diffusion coefficients of the polymer mixture can be estimated under certain conditions. Illustrative data and calculations of the moments using an IBM 650 machine are reported for some lignin sulfonate polymers. Estimates also are given of the corresponding weight distributions of diffusion coefficients and of molecular weights of the lignin sulfonates.

Introduction

In the study of lignins and other polymers, it is often of importance to ascertain the mean molecular weights and also the distribution in molecular weights of the components of a given preparation. In this Laboratory some information on the molecular weights of lignin sulfonates has been obtained using diffusion[3] and light scattering methods[4] and, in several cases, preparations have been fractionated by reprecipitation procedures and the mean molecular weights of the resultant fractions have been estimated to secure information

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(1) Extracted in part from a Dissertation submitted by Jovan Moacanin in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Washington in 1956.

(2) Extracted in part from the Thesis submitted by Harold Nelson in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at the University of Washington in 1957.

(3) V. F. Felicetta, A. E. Markham, Q. P. Peniston and J. L. McCarthy, THIS JOURNAL, **71**, 2879 (1949).

(4) J. Moacanin, V. F. Felicetta, W. Haller and J. L. McCarthy, *ibid.*, **77**, 3470 (1955).