when n is an odd integer and

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

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

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

Substitution for I from equation 7 and rearrangement gives

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

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

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

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

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

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

$$\mu'_{D_n} = \frac{n}{2^n t^{n/2} G}\,\mu'_{c\,n-1} \qquad (17)$$

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

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

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

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

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

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.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM PULP MILLS RESEARCH AND DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

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).

on the distribution in molecular weights.[5] These procedures seem to have given moderately reliable results judging from the approximate agreement found between our molecular weight results and those obtained in careful independent investigations by Gordon and Mason[6] using osmotic pressure methods.

However, since the several fractionation and diffusion procedures are tedious to carry out and, moreover, do not provide information as to the distribution in molecular weights within a finally separated fraction, we have given consideration to the possibility of using diffusion measurements for estimating the distribution, as well as the mean value, of diffusion coefficients or molecular weight. Studies in this field have been conducted by Lamm,[7] Gralén[8] and Daune and Freund[9] who have recorded equations for computing certain statistical moments and mean diffusion coefficients for polydisperse systems using diffusion data obtained by the Lamm scale method. In this Laboratory,[10] somewhat similar equations have been developed for treating diffusion data obtained by absorbance measurements.

The purpose of this report is to illustrate the application of these relationships and of machine calculation methods for the estimation of the distribution in diffusion coefficients in polymers. Some numerical results are given which were obtained by use of a particular diffusion procedure with lignin sulfonate preparations and these results serve to indicate the rather high degree of accuracy required in the experimental measurements and the data processing procedures if satisfactory estimates of distributions are to be attained.

Experimentation and Calculation

Materials for Diffusion.—Diffusion experiments were conducted using the pure substance vanillin (m.p. 81.5°) and also lignin sulfonates prepared from a previously described[4] sample of Western Hemlock (*Tsuga heterophylla*) wood meal. Delignification of this wood meal nearly to completion was carried out by sealing in glass bombs a total of 164 g. of air-dried extracted wood meal together with 1000 ml. of an aqueous sulfurous acid–sodium bisulfite solution (50 g. of SO_2/l. and 9.67 g. of Na_2O/l. or 4% "free SO_2" and 1% combined SO_2"), heating for 4.5 hr. at 135°, then cooling and opening the bombs. The contents of the bombs were combined and the cellulosic residue was filtered off, washed with distilled water, air-dried, weighed and found to be 49% of the air-dried wood meal.

The resulting solution was exhaustively dialyzed[4] for 160 hr. at which time about 36% of the initial material absorbing 2800 Å. radiation had passed through the membrane. The resulting solution of purified non-dialyzable sodium lignin sulfonates contained 9.77 g. of total solids/l. exhibiting 12.1 l./g. cm. absorptivity at 2800 Å.

An aliquot (470 ml.) containing 4.7 g. of these non-dialyzable sodium lignin sulfonates was vacuum evaporated to 100 ml. and then placed in a one liter bottle together with 4.6 g. of C.P. NaCl. An ethanol solution (680 ml. at 95% by volume) was added dropwise with vigorous stirring and over a 40-minute period at about 25° and, after stirring 15 minutes more, the solution was poured off and called fraction 1. The remaining heavy phase was redissolved in 55 ml. of a salt solution containing 1.8 g. of NaCl. Then 250 ml. of 95% ethanol was added as before and the solution resulting was called fraction 2. The heavy phase was again redissolved in 50 ml. of a salt solution containing 1.2 g. of NaCl, and 165 ml. of 95% ethanol was used for the precipitation. The solution resulting was called fraction 3 and the heavy phase was dissolved in water and called fraction 4. Ethanol was evaporated from each fraction and the resulting four aqueous solutions were saturated with toluene and stored at 4° to minimize microörganism action. Prior to use for diffusion measurements, toluene was removed by vacuum evaporation.

Apparatus and Procedure for Diffusion.—Solution-to-gel-diffusion cells were made from two quartz glass microscope slides separated by ordinary glass spacers about 2.5 mm. thick as previously described[3] and with the open end carefully squared with respect to one side. An experiment was conducted by permitting a solute which absorbs ultraviolet radiation to diffuse for an appropriate time from a buffered aqueous solution into an agar gel in the cell, placing the cell into a special holder[11] in a Beckman Model DU spectrophotometer equipped with a photomultiplier attachment[12] and then observing the absorbance or solute concentration at several distances from the phase boundary into the gel. The buffered aqueous solution and the agar gel were 1.0 *M* in NaCl, 0.10 *M* in NaH_2PO_4 and 0.02 *N* in NaOH.

Since the available "Difco" powdered agar was found to contain substances which absorbed ultraviolet radiation and were soluble and tended to diffuse through the gel out of the cell, the agar was purified by stirring it for 1 hr. suspended in cold distilled water, and then straining off the agar using a fine mesh cloth and rejecting the extract solution. Five such cold water extractions were carried out and these were followed by continuous extraction with 60° water until agar swelling clogged the cloth filter. Then the water was replaced by ethanol and this by ether to yield a fluffy dry agar readily soluble in hot water and providing a satisfactory gel at a concentration of 0.4% in the aqueous salt solution usually used for diffusion.

After thoroughly cleaning the diffusion cells and vacuum drying them in a desiccator over $CaCl_2$ to avoid dust and lint, the cells were filled to overflowing with a hot clear 0.4% agar solution in the aqueous buffer system prepared by heating the agar–buffer solution for five minutes in a preheated autoclave at 10 p.s.i.g. steam jacket pressure. After 20 minutes at room temperature in a humid container, the agar has set firmly and a sharp boundary was formed by slicing the agar even with the end of the cell by use of a razor blade. Immediately, the cell was inverted, attached to a split cork and a bottle so that the cell dipped to a depth of about 5 mm. into 70 ml. of the aqueous buffered salt solutions containing the solute to diffuse. With lignin sulfonates and vanillin, the solute concentration was about 500 and 50 mg./l., respectively. Bottles and cells were mounted in a shaking rack of slow period in a 25 ± 0.1° water-bath for diffusion periods of one to two days. Then the cells were removed individually, wiped clean and dry with lens paper without disturbing the gel interface, and inserted into the cell holder of the scanning attachment[11] which was placed in the cell chamber of a Beckman model DU spectrophotometer equipped with a photomultiplier arrangement. These operations were carried out in a minute or less to minimize drying of the boundary. The spectrophotometer was set for zero absorbance at 2800 Å. against pure agar gel as found in the cell at a "standard position" 30 mm. or more from the interface boundary and at 33.2 mm. scale reading in present experiments. Absorbance readings were taken beginning at a position about 1 mm. from the boundary and then continued at positions corresponding to each complete turn of the vernier dial (0.061 to 0.065 cm. intervals with the present apparatus[11]) until absorption became negligible. The total of 25 or 30 readings taken as illustrated in Table I were completed in less

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(5) (a) V. F. Felicetta, A. Ahola and J. L. McCarthy, THIS JOURNAL, **78**, 1899 (1956); (b) E. Nokihara, M. Jean Tuttle, V. F. Felicetta and J. L. McCarthy, *ibid.*, **79**, 4495 (1957); (c) V. F. Felicetta and J. L. McCarthy, *ibid.*, **79**, 4499 (1957).

(6) J. L. Gordon and S. G. Mason, *Can. J. Chem.*, **33**, 1477 (1955).

(7) (a) O. Lamm, *Nova Acta Reg. Soc. Sci. Upsaliensis*, [IV] **10**, No 6 (1937); (b) "Die Methoden der Fermentforschung," edited by E. Bamann and K. Myrbäck, Leipzig, 1940, p. 659.

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

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(10) J. Moacanin, V. F. Felicetta and J. L. McCarthy, THIS JOURNAL, **81**, 2052 (1959).

(11) E. Back, V. F. Felicetta and J. L. McCarthy, *Anal. Chem.*, **29**, 1903 (1957).

(12) Instruction Manual 305-A, Beckman Instruments, Inc., Fullerton, California.

TABLE I

DIFFUSION DATA AND CORRECTIONS FOR NON-DIALYZABLE LIGNIN SULFONATE SAMPLE U-208[a]

Position		A_x					
Turns	Arbitrary scale, cm.	Obsd.	After glass corr.	After blank corr.	After path length corr.	After slit width corr.	$\frac{A_x}{2A_0}$
(−1.523)	(0.370)		(estimated boundary position)				(0.500)
0	0.466	1.104	1.091	1.108	1.090	1.093	.426[b]
1		0.978	0.978	0.994	0.978	0.981	....
2	.594	.858	.858	.873	.877	.880	.334[b]
3		.743	.743	.757	.772	.775	....
4	.720	.640	.640	.653	.661	.663	.250[b]
5		.544	.545	.557	.564	.566	....
6	.847	.456	.457	.468	.474	.476	.179[b]
7		.384	.384	.394	.398	.400	....
8	.974	.322	.322	.332	.335	.336	.126
9		.267	.266	.275	.277	.278	....
10	1.100	.219	.219	.227	.229	.230	.086
11		.179	.180	.188	.189	.190	....
12	1.226	.146	.147	.155	.156	.157	.059
13		.119	.119	.126	.127	.128	....
14	1.354	.095	.096	.103	.104	.104	.038
15		.076	.076	.082	.082	.082	....
16	1.480	.060	.058	.064	.064	.064	.024
17		.047	.047	.053	.053	.053	....
18	1.606	.036	.036	.042	.042	.042	.015[c]
19		.028	.028	.034	.034	.034	....
20	1.732	.022	.022	.026	.026	.026	.010[c]
21		.017	.014	.018	.018	.018	....
22	1.858	.013	.013	.017	.017	.017	.006[c]
23		.011	.011	.015	.015	.015	
24	—	.008	.008	.012	.012	.012	
25		.006	.007	.009	.009	.009	

[a] Solution absorbance = A_0 = 1.352; diffusion time = 35 hr. and 53 min. [b] Interpolated using first degree equation for probability plot in this region. [c] Interpolated using a linear probability plot in this region.

than ten minutes. Spectrophotometer drift did not exceed 0.001 absorbance per five minutes. Elapsed time between the start of diffusion and the removal of the cell from the solution for scanning was taken as the diffusion time.

After completion of scanning, the diffusion cell was cleaned, filled with buffered 1 *M* NaCl solution, placed in a vertical position in the spectrophotometer which was then balanced. The buffered 1 *M* NaCl solution was replaced by the lignin sulfonate solution after dilution if necessary, and the solution absorbance A_0 was determined. For each set of diffusion experiments, a "blank" diffusion to evaluate the agar correction required was carried out using the entire above-described procedure except that no sample was added to the solution contained in the cell bottle.

Correction of Absorbance Observations.—Since the thickness of the glass walls in each diffusion cell varied somewhat depending upon distance from the boundary end of the cell, a "glass correction" cell calibration was established by carefully cleaning the cell, placing it in the cell holder, positioning the cell at the "standard" location at 33.2 mm. scale reading and setting the spectrophotometer to zero at this position, and then determining absorbances at various specific positions through the cell. After reversal of sign, these absorbances were applied as additive corrections directly to diffusion measurements as illustrated in Table I.

Since substances absorbing ultraviolet radiation tend to diffuse out of the agar phase, a "blank correction" was evaluated for each particular batch of agar by using the absorbance-boundary distance data obtained in a "blank" diffusion, applying the "glass corrections" to these absorbances and smoothing the resulting values which were then reversed in sign and applied as additive corrections (Table I).

Since the light path length through a cell varied with position, "path corrections" were evaluated by filling each cell with an agar solution containing the buffer-salt mixture and also an absorbing substance such as potassium acid phthalate, dipping the cells into an aqueous solution containing the buffer-salt mixture and also an absorbing substance at the same concentration, and allowing diffusion to proceed for two days. A cell then was removed and scanned as usual after setting the spectrophotometer to zero at the "standard" position. Absorbance A_0 of the solution of the absorbing substance *versus* distilled water was measured with the cell standing upright as noted above. "Glass" and "blank" corrections were applied to obtain corrected path length absorbances ΔA_{xp}. Thus the path length at position x in the cell was $(A_0 + \Delta A_{xp})/A_0$ relative to the "standard" cell position. The quotient obtained by dividing this ratio into the corresponding absorbance obtained above provided diffusion measurements corrected for variable path length (Table I).

Corrections for the finite width of the scanning beam and for varying radiation intensity across this beam have been made for the presently reported data by procedures discussed elsewhere.[13]

Determination of the "Boundary" Position.—Usually, corrected absorbance measurements A_x, at positions corresponding to 3, 4, 5 and 6 dial turns were divided by the solution absorbance A_0, to give absorbance ratios. These were subtracted from one and then the values of the standardized variable β in the corresponding error functions

$$\left[1 - \frac{A_x}{A_0}\right] = \operatorname{erf} \beta = \frac{2}{\sqrt{\pi}} \int_0^{\beta} e^{-y^2}\, dy$$

were obtained from tabulations of the error function or the probability integral.[14] By a least squares fitting procedure[15] applied to values of β *versus* position expressed as dial turns 3, 4, 5 and 6, there was obtained a first degree equation. The position of the boundary expressed as dial turns was now

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(13) E. Back, V. F. Felicetta and J. L. McCarthy, *Anal. Chem.*, **30**, 1875 (1958).

(14) (a) "Tables of the Error Function and its Derivative," National Bureau of Standards, Applied Mathematics Series 41, Washington, D. C., 1954; (b) "Tables of the Error Function and of its First Twenty Derivatives," Annals of the Computation Laboratory of Harvard University, Vol. XXIII, Harvard University Press, 1952.

(15) J. B. Scarborough, "Numerical Mathematical Analysis," John Hopkins Press, Baltimore, Md., 1950, pp. 451-454.

calculated by solving the equation for the case $\beta = 0$. The values of β corresponding to the positions of dial turns 3, 4, 5 and 6 also were calculated and then converted, using available tabulations,[14] to corresponding values of $[1 - A_x/A_0]$ and finally to the smoothed values of $A_x/2A_0$ shown in Table I for the specified positions.

The "Tail" Region.—Using "probability" ruled graph paper (Keuffel and Esser No. 359-23), a plot of $A_x/2A_0$ *versus* integral dial turn positions 18 through 25 was prepared. The best straight line was drawn through the points and smoothed values for $A_x/2A_0$ at positions of 18, 20 and 22 turns were taken for use in the "PALS" program. Smoothed values A_x/A_0 at the positions of 21, 22 and 23 turns also were taken and used with the equation

$$(\text{Slope})_{s_L} = \frac{\Delta\left(\frac{A_x}{A_0}\right)_{22}}{\Delta x} = \frac{\left[\left(\frac{A_x}{A_0}\right)_{22} - \left(\frac{A_x}{A_0}\right)_{21}\right] + \left[\left(\frac{A_x}{A_0}\right)_{23} - \left(\frac{A_x}{A_0}\right)_{22}\right]}{(2)(0.0633)} \quad (1)$$

to estimate the rate of change of concentration ratio with distance at the position of 22 turns for use in the "MEDD" program.

Machine Calculations.—An I.B.M. 650 Digital Computing Machine with accessories was used to process the data. The corrected $A_x/2A_0$ data (Table I) were fitted by the method of least squares with a fifth degree polynomial using an available machine program, PALS,[16] adapted in detail to the present purpose by Nelson.[17]

The first point taken was the boundary position, $A_x/2A_0 = 0.5$, the next was at the position corresponding to zero turns, and the remaining points were taken at the positions of even numbers of turns up to, for most of the calculations, 13 equally weighted points which correspond to $s_L = 1.858$ on the arbitrary scale of position. The computing time and residual variance associated with this fitting for several different numbers of points and degrees for the polynomials are discussed elsewhere.[18]

The polynomial equation and other data were used with previously discussed relationships to calculate statistical moments and distribution of diffusion coefficients. Because of the tedious nature of the calculations, an I.B.M. 650 machine computational program called "MEDD" (*i.e.*, moment evaluation for distribution in diffusivities) has been written by Nelson[17] and was used in the present study. The parameters needed for this program are: six coefficients for the fitted polynomial; δ(cm.) = the distance to the boundary from zero on the arbitrary scale; s_L (cm.) = the upper limit of the PALS fitting of the polynomial to smoothed data and of its integration in terms of the arbitrary abscissa scale (usually at 1.858); A_0 = actual absorbancy at boundary; t seconds = time of diffusion; $\beta_L = x/\sqrt{4D_Lt}$ = a dimensionless group; $[\mathrm{d}A_x/\mathrm{d}s]_{s_L}$ cm.$^{-1}$ = slope of absorbance–position curve at upper limit of polynomial integration; and $E_L = e^{-\beta^2_L}$.

To estimate the moment contributions arising from the "tail" region for which observations are unreliable or unavailable, input data with the characteristics arising when only a single solute of diffusivity D_L diffuses were assumed for this region. The appropriate parameters were obtained by first estimating by graphical means the slope of the corrected $A_x/2A_0$ *vs.* distance plot at the position s_L, and then one of the needed quantities was calculated

$$[\mathrm{d}A_x/\mathrm{d}s]_{s_L} = (\text{slope})_{s_L}(A_0) \quad (2)$$

A certain function of β_L called R_L also then was obtained as

$$R_L = \frac{(X_L)(\text{slope})_{s_L}}{(2)(A_x/2A_0)_{s_L}} \quad (3)$$

where $x_L = s_L - \delta$. Now by definition R is related to β by the equation

$$R = \frac{-\left(\frac{2}{\sqrt{\pi}}e^{-\beta^2}\right)\beta}{\left(1 - \frac{2}{\sqrt{\pi}}\int_0^\beta e^{-y^2}\,\mathrm{d}y\right)} \quad (4)$$

and in present work it was found convenient to use error function tables[14] to establish several corresponding numerical values for β and R, to construct a large scale graph of these values and then to interpolate from this graph the needed value of β_L from the value at hand for R_L.

The first machine calculation in the MEDD program is a transformation of polynomial coefficients to an origin of zero by solving simultaneous equations involving the coefficients and δ. The next calculation is integration of the polynomial equations to obtain four "partial moments" about the origin, $\bar{\mu}'_{cn}$; for the concentration distribution curve from the boundary to $x_L = s_L - \delta$ as

$$\bar{\mu}'_{c0} = 2\int_0^{x_L} x^0\left(\frac{C_x}{2C_0}\right)\mathrm{d}x \quad (5)$$

$$\bar{\mu}'_{c1} = 2\int_0^{x_L} x^1\left(\frac{C_x}{2C_0}\right)\mathrm{d}x \quad (6)$$

$$\bar{\mu}'_{c2} = 2\int_0^{x_L} x^2\left(\frac{C_x}{2C_0}\right)\mathrm{d}x \quad (7)$$

$$\bar{\mu}'_{c3} = 2\int_0^{x_L} x^3\left(\frac{C_x}{2C_0}\right)\mathrm{d}x \quad (8)$$

Evaluation of the "tail" contributions to these moments is done by use of the relation

$$\frac{C_x}{2C_0} = \frac{C_0'}{2C_0} - \frac{C_0'}{V_LC_0\sqrt{\pi}}\int_0^x e^{-\frac{x^2}{V_L}}\mathrm{d}x \quad (9)$$

where C'_0 is the hypothetical boundary concentration which would be associated with monodisperse material, $V_L = \sqrt{4D_Lt}$, and $x_L/V_L = \beta_L$, and the integral is evaluated by the series

$$\int_0^x e^{-\frac{x^2}{V_L^2}}\mathrm{d}x = \left[x - \frac{kx^3}{3} + \frac{k^2x^5}{5(2!)} - \frac{k^3x^7}{7(3!)} + \cdots + \frac{k^nx^{2n+1}(-1)^n}{(2n+1)(n!)}\right] \quad (10)$$

where $k = \frac{1}{V_L^2}$.

Using Simpson's Rule, additional distance effects are evaluated incrementally and added to each $\bar{\mu}'_{cn}$ until the change in the total μ'_{cn} becomes less than 0.1% of μ'_{c3}.

In general, moment contributions from the "tail" region for the third moments, *i.e.*, $\mu'_{c3} - \bar{\mu}'_{c3}$, are preferably around one-fourth of μ'_{c3}, and this relationship is secured by appropriate selection of the time period allowed for diffusion. Inadequate separation of the diffusing species occurs if the time is too short, whereas the influence of the unreliable assumption about the tail region may be unnecessarily large if the time is too long.

The concentration distribution moments are converted to moments about the origin for the distribution of $D^{1/2}$ and these moments are defined as

$$\mu'_{Dn} = \Sigma(w_i)(D_i^{1/2})^n \quad (11)$$

where w_i = weight fraction present of the ith polymer species of diffusivity D_i, and n = positive integer order of the moment. The calculation of the moments for the distribution of diffusion coefficients is carried out using equations which were derived in another paper.[10]

Diffusion moments about the origin are converted to diffusion moments about the mean, μ_{Dn}, by the relations

$$\mu_{D2} = \mu'_{D2} - (\mu'_{D1})^2 \quad (12)$$

$$\mu_{D3} = \mu'_{D3} - 3\mu'_{D1}\mu'_{D2} + 2(\mu'_{D1})^3 \quad (13)$$

$$\mu_{D4} = \mu'_{D4} - 4\mu'_{D1}\,\mu'_{D3} + 6(\mu'_{D1})^2\mu'_{D2} - 3(\mu'_{D1})^4 \quad (14)$$

From moments about the mean two dimensionless moment ratios are evaluated, as

$$a_3 = \frac{\mu_{D3}}{\mu_{D2}{}^{3/2}} \quad \text{and} \quad a_4 = \frac{\mu_{D4}}{\mu^2_{D2}} - 3 \quad (15)$$

and from these the distribution of $D^{1/2}$ or D is estimated by

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(16) R. E. van Holdt and R. J. Brosseau, "Polynomial Approximation by Least Squares," Univ. of California Radiation Laboratory, Publication UCRL-4700 (1956).

(17) H. Nelson, Thesis, M.S. in Chem. Engr., University of Washington, 1957.

(18) H. Nelson and J. L. McCarthy, unpublished work.

TABLE II

SUMMARY OF MOMENT DATA FOR VANILLIN AND LIGNIN SULFONATE PREPARATIONS

Expt.	Sample[a]	μ'_{D1} $\times 10^3$, cm. sec.$^{-1/2}$	μ'_{D2} $\times 10^6$, cm.^{2} sec.$^{-1}$	μ'_{D3} $\times 10^9$, cm.^{3} sec.$^{-3/2}$	μ'_{D4} $\times 10^{12}$, cm.^{4} sec.$^{-2}$	μ_{D2} $\times 10^9$, cm.^{2} sec.$^{-1}$	μ_{D3} $\times 10^{12}$, cm.^{3} sec.$^{-3/2}$	μ_{D4} $\times 10^{15}$, cm.^{4} sec.$^{-2}$
1058	Van	2.64	6.96	18.4	48.5	− 1	− 1	−1
1060	Van	2.71	7.35	19.9	54.0	− 1	+ 2	0
U-208	LS	1.072	1.206	1.422	1.744	+56	+ 8	0
U-209	LS	1.077	1.213	1.430	1.751	+53	+ 9	−2
U-211	LS	1.095	1.241	1.455	1.756	+42	+ 5	−3
U-213	LS	1.078	1.218	1.446	1.795	+56	+12	+5
A-01	LS-1	1.268	1.651	2.201	2.988	+44	− 3	+1
B-01	LS-1	1.308	1.729	2.318	3.158	+18	+10	−3
A-02	LS-2	1.122	1.281	1.489	1.763	+22	+ 3	+2
B-02	LS-2	1.116	1.265	1.454	1.692	+20	− 2	0
A-03	LS-3	0.986	1.006	1.065	1.168	+33	+ 8	−1
B-03	LS-3	1.017	1.052	1.139	1.139	+19	+31	+6
A-04	LS-4	0.805	0.663	0.562	0.489	+16	+ 3	−1
B-04	LS-4	0.815	0.685	0.597	0.541	+21	+ 5	+1

[a] LS = unfractionated non-dialyzable lignin sulfonate preparation. LS-1, LS-2, LS-3 and LS-4 = individual fractions of LS. Van. = vanillin.

use of the Orani–Charlier series of Type A[19−21] for which the first three terms are

$$f(Z) = \phi(Z) - \frac{a_3}{3!}\phi^{111}(Z) + \frac{a_4}{4!}\phi^{1V}(Z) \qquad (16)$$

where: $f(Z)$ = a frequency function of Z; $\phi(Z) = (1/\sqrt{2\pi})(e^{-Z^2/2})$ = the normal frequency function of Z; $\phi^{111}(Z)$ and $\phi^{1V}(Z)$ = third and fourth derivatives of $\phi(Z)$; a_3 and a_4 are asymmetry and kurtosis coefficients defined by equation 15, and the standardized variable is

$$Z_i = \frac{D_i^{1/2} - \mu'_{D1}}{\mu_{D2}^{1/2}} \qquad (17)$$

For present purposes, it is thought convenient to secure the results as an integrated or cumulative distribution, $F(Z)$, such that

$$F(Z) = \int_{-\infty}^{z} f(Z)\mathrm{d}Z \qquad (18)$$

which for equation 16 is

$$F(Z_i) = {}^1/_2 + \int_0^z \phi(Z_i)\mathrm{d}Z - \left(\frac{a_3}{3!}\right)(\phi^{11}(Zi)) + \left(\frac{a_4}{4!}\right)(\phi^{111}(Zi)) \qquad (19)$$

where $\phi^{11}(Z)$ and $\phi^{111}(Z)$ = second and third derivatives of $\phi(Z)$. To obtain representations of a weight fraction cumulative distribution W_i running from zero to about one, values of $F(Z_i)$ are adjusted with a scale displacement constant $F(Z = -\infty)$ given by

$$F(Z = -\infty) = -\left(\frac{a_3}{3!}\right)(\phi^{11}Zi) \qquad (20)$$

and

$$W_i = F(Z_i) - F(Z = -\infty) \qquad (21)$$

Values of D_i corresponding to W_i values are found by rearranging and then solving equation 17 using the respective values of Z_i together with the approximate first moment about the origin and second moment about the mean

$$D_i = [(Z_i)(\mu_{D2}^{1/2}) + \mu'_{D1}]^2 \qquad (22)$$

The MEDD program contains seventeen values of Z_i over the range from minus to plus infinity along with corresponding derivative functions so that seventeen pairs of values of cumulative weight fraction of polymer and diffusion coefficient are computed. Each set of diffusion distribution calculations requires about 3 minutes of IBM 650 computing time exclusive of deck load time.

Discussion

To utilize the presently discussed procedure illustrating polymolecularity estimation, some major necessary assumptions are: (a) that the diffusing solutes comprise a large number of different polymeric species, (b) that these are distributed so as to provide a unimodal frequency function, (c) that the absorptivity of the solutes is a constant substantially independent of diffusion coefficient and (d) that the diffusion is substantially not concentration-dependent. Prior studies in this Laboratory seem to provide evidence in support of (a), (b) and (c) for lignin sulfonates.[5] In present work, the absorptivity of lignin sulfonates was investigated and found to be slightly decreased by increased ionic strength, but when the concentration of sodium chloride was held constant at one molar, a linear absorbance–concentration relationship was found to exist up to 1.1 absorbance and 0.5 gram sodium lignin sulfonate per liter, so experiments were conducted within this range assuming the validity of Beer's law. The low levels of lignin sulfonate concentrations used are believed to provide for the approximate validity of (d) although methods are available to treat concentration-dependence situations for certain cases.[22]

The location of the solution–gel boundary must be established nearly exactly if useful distribution estimations are to be made. In the present study much effort was made to locate the boundary by a direct measurement in various ways but satisfactory results could not be obtained. Thus the above-described extrapolation method was accepted based on the fact that the curvature of the concentration–distance function for a pure substance or for a mixture of solutes decreases as the boundary is approached and a straight line relationship is approximated near the boundary. The finding that the values of the variance of μ_{D2} for the pure substance vanillin are nearly zero (Table

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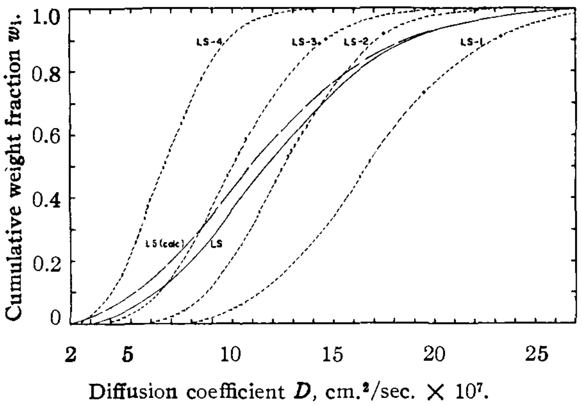

Fig. 1.—Distribution of diffusion coefficients estimated for certain lignin sulfonate preparations.

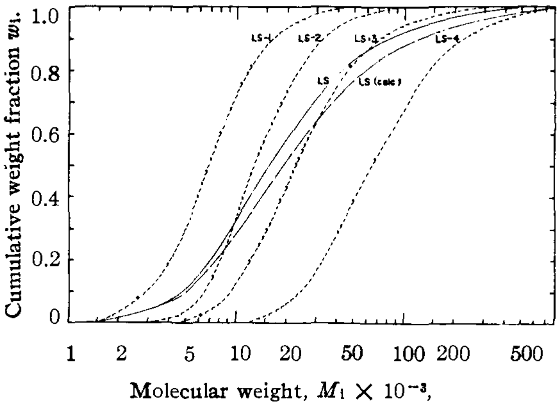

Fig. 2.—Distribution of molecular weights estimated for certain lignin sulfonate preparations.

II) is believed to provide support for the approximate validity of the presently used method for location of the boundary and also for the absence of substantial concentration dependence in the diffusion of vanillin under present conditions at least.

The moments obtained for the lignin sulfonates investigated are summarized in Table II. Four replicate experiments and calculations were carried out to estimate the distributions in a certain nondialyzable lignin sulfonate preparation designated as LS. Moderately good reproducibility is indicated for the weight average diffusion coefficient μ'_{D2} and for the variance μ_{D2} of LS but the usefulness is questionable of the higher moments μ_{D3} and μ_{D4}. The LS sample was separated by reprecipitation[4] into four fractions and duplicate estimates of μ'_{D2} and μ_{D2} agreed satisfactorily for fractions LS-2 and LS-4, but less well for fractions LS-1 and LS-3 which did not give representative results.

The weight fraction of LS which was obtained in each of the four fractions is shown in Table III and indicates that only about 93% recovery of the original material was secured. Assuming that the loss was distributed among the fractions in proportion to the weight fraction recovered, the average moments about the origin are used to compute the weighted average moments, and from these the variance associated with the unfractionated LS sample was calculated using equation 12. Calculated and experimentally found values for LS were in rough agreement, *i.e.*, 1.15 *versus* 1.22 × 10^{-6} cm.^{2} sec.$^{-1}$ for the weight average diffusion coefficient and 62 *versus* 52 × 10^{-9} cm.^{2} sec.$^{-1}$ for the variance, respectively.

TABLE III

MEAN MOMENT RELATIONSHIPS FOR LIGNIN SULFONATE PREPARATIONS

Sample	Wt. fraction	μ'_{D1} × 10^3, cm. sec.$^{-1/2}$	μ'_{D2} × 10^6, cm.^{2} sec.$^{-1}$	μ_{D2} × 10^9, cm.^{2} sec.$^{-1}$	a_3	a_4
LS-1	0.27	1.29	1.69	31	0.6	−4.6
LS-2	.17	1.12	1.27	21	0.2	−1.0
LS-3	.18	1.00	1.03	26	4.7	+0.6
LS-4	.31	0.81	0.67	18	1.6	−4.1
Weighted sum of LS fractions	0.93	1.04	1.15	62	0.3	−4.3
LS	1.00	1.08	1.22	52	0.72	−3.2

For a normal distribution curve, the asymmetry and kurtosis coefficients, a_3 and a_4, are zero. For other unimodal distribution curves, a_2 and a_3 may be positive or negative. If a_3 is not zero, the distribution curve is asymmetric. If a_4 is not zero and is positive, the curve relative to the normal frequency distribution curve is tall and slim or "leptokurtic," but if a_4 is negative, the curve is flattened and squat or "platykurtic." Construction of distribution curves from moments using the Gram–Charlier series is conducted using a_3 and a_4 and limitations of this treatment are found in the characteristics of the series itself (20, 21) and in the precision with which the higher moments and thus the coefficients such as a_3 and a_4 can be estimated since unreliable or erroneous values may give rise to modifications in the normal distribution which can become larger than the function itself.

In present work mean values found for a_3 and a_4 are not significant for vanillin and probably do not indicate a significant departure from a normal distribution for the lignin sulfonates. Studies are continuing in this Laboratory to verify and interpret this finding.

Assuming normal distributions for the lignin sulfonate preparations LS, LS-1, LS-2, LS-3 and LS-4 and using the mean values of μ'_{D1}, and μ_{D2} given in Table III, the several distributions in diffusion coefficients have been calculated and are represented in Fig. 1. There is shown also the distribution estimated for LS by calculation from the results found for the four fractions and, in spite of the difficulties with yields and with measurements on LS-1 and LS-3, this calculated result is in moderately good agreement with that found experimentally for LS.

To represent the distributions in terms of molecular weights, some function relating diffusion coefficient with molecular weight must be available. For lignin sulfonates, diffusion and light scattering studies have led to an empirical relationship of the form $M = a_m D^{-b_m}$ where the constants a_m and b_m have values of 3.6 × 10^{-14} and 8.0 × 10^{-11} and of 3.0 and 2.41, respectively, when the diffusion coefficient is above or below 20 × 10^{-7} cm.^{2}/sec. *i.e.*, when the molecular weight is below or above about four thousand.[23] On this basis, molecular weights have been computed from the diffusion coefficients shown in Fig. 1 and the resultant estimated molecular weight distribution curves are illustrated in Fig. 2.

Although rather accurate measurements and calculations are necessary for satisfactory estimation of distributions, it appears that approaches of the above-described type often may be found useful in studies of polymers. Kinetic studies of changes in distributions of diffusion coefficients for lignin sulfonates are proceeding utilizing the described theory and methods.

SEATTLE, WASHINGTON

[23] These constants for the molecular weight–diffusion coefficient exponential relationships were obtained with fractions prepared by a previously described procedure[4] using weight average molecular weights which were estimated previously by a light scattering procedure[4] and using weight average diffusion coefficients which have recently been newly determined in the presently used buffered 1 *M* NaCl solution.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND SHELL DEVELOPMENT COMPANY]

Direct Dimerization of Terminal Olefins by Ionizing Radiation[1,2]

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Terminal olefins were irradiated in liquid phase with high energy electrons and γ-rays to study the mechanism of radiolysis. Low molecular weight polymers were the principal products. The dimeric fraction was mainly monoölefin, with small amounts of diolefins, paraffins and cyclic material. Hydrogenation of the dimer yielded *n*-dodecane (45%) and 5-methylundecane (35%). Ozonolysis of the dimer fraction and identification of the isolated acids provided a pattern consistent with the location of the double bond in any of several of the possible locations in the simple carbon skeletons. The contrast between these structures and those obtained in free radical-induced reactions of terminal olefins provides evidence against a free radical mechanism. An ion-molecule mechanism is proposed to explain these facts; it is postulated that the molecule ion reacts directly with a molecule to form a carbon–carbon bond utilizing the pi electrons of the molecule. The energy-rich complex so formed is held together in the liquid cage until its energy is dissipated by collision.

Although the nature of the fundamental processes in the radiolysis of saturated hydrocarbons has been investigated in some detail, that of simple olefins has received little attention. Both free radicals[3-6] and ions[7-11] have been suggested as intermediates in the radiolysis of paraffins. In order to investigate the relative importance of these intermediates in the radiolysis of simple olefins, 1-hexene and 1-octene have been irradiated and the products analyzed and compared with those obtained from radical-induced reactions of simple olefins.[12,13]

Experimental

Purification of Starting Materials.—The olefins (Pure Grade, 99 mole % minimum, Phillips Petroleum Co.) were fractionally distilled over sodium under nitrogen. The purified olefins did not give a test for peroxides. The 1-hexene contained 0.01% *n*-hexane plus 0.06% other unidentified hydrocarbons.

Irradiation with γ-Rays.—The source of γ-rays was the High Level Irradiation Facility of the Argonne National Laboratory. The olefin was thoroughly degassed under vacuum, distilled into a 200-ml. irradiation flask, and the flask was sealed *in vacuo*. Radiation dosage was determined by ferrous sulfate dosimetry.

Irradiation with Electrons.—The source of electrons was a 3 Mev. Van de Graaff accelerator. Irradiation was conducted in an all-glass apparatus consisting of an irradiation cell with 1 mm. thick window, a reservoir, a −78° reflux condenser and a gas collector. The capacity of the system was 150 ml. The olefin was circulated through the irradiation cell by a magnetic centrifugal pump, and the olefin was cooled by a heat exchanger in the circuit. The beam current used was 3 microamperes. Dosage was determined by ceric ion dosimetry with the identical experimental arrangement. Dimensions were such that the electron beam was completely absorbed in window plus fluid.

Analysis.—In the electron irradiation experiments, the gaseous products collected were analyzed by mass spectrometry. In the γ-ray irradiation experiments, the gaseous products were removed on a vacuum line and analyzed according to the procedure used by Kharasch, Lewis and Reynolds.[14]

The remainder of the reaction mixture was distilled at 100 mm. and room temperature. The fraction thus collected in the Dry Ice trap was further fractionated through a Podbielniak Hyper-Cal column. The 2% forecut and the remainder were separately analyzed by gas chromatography with a dimethyl sulfolane column (50' × $^1/_4$") for the detection of C_5 and C_7 hydrocarbons, hexane, hexadienes and 2- and 3-hexenes.

The high-boiling material was distilled through a tantalum spiral column (24" × $^1/_4$"). These several fractions were collected: fraction I, b.p. 87–92° (20 mm.), $n^{20}\text{D}$ 1.4350, mol. wt., 169; fraction II, b.p. 76–80° (0.1 mm.), $n^{20}\text{D}$ 1.4490, mol. wt., 250; fraction III, b.p. 117–120° (0.05 mm.), $n^{20}\text{D}$ 1.4572, mol. wt., 330. The fractions were confirmed by mass spectrometric analyses to be dimers, trimers and tetramers, respectively.

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[1] (a) This work was supported in part by the United States Air Force under contract with the University of Chicago (Contract No. AF 33(616)-3875) monitored by Aeronautical Research Laboratory (WCRRC) Wright Air Development Center. (b) Presented at the 134th Meeting of the American Chemical Society, Chicago, Illinois.

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