Extraparticle Diffusional Effects in Gel Permeation Chromatography.   II. Experimental Results

A. OUANO* and J. A. BIESENBERGER, *Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030*

Synopsis

Experiments coupled with a systems analysis were conducted on chromatogram dispersion, or zone broadening, in gel permeation chromatography (GPC).   Three components of a Waters Associates Model 200 chromatograph, each of which is a potential cause of dispersion, were considered; these are: the packed column, with extraparticle dispersion only; the empty tubing, between pump and columns, columns and detector, etc.; and the detection system, viz., the differential refractometer cell.   Toluene solvent was used and the solutes whose dispersion was studied included orthodichlorobenzene (ODCB) and narrow-molecular-weight polystyrene standards having molecular weights of 900, 20,400, 51,000, 97,200, and 160,000.   Nonporous glass beads, 50 μ in diameter, were used as column packing.   Two diameters, 1 mm and 0.5 mm, of stainless steel tubing were studied.   In addition to the usual rectangular pulse sample injection, a step input mode for solute introduction was also used.   The empty tubing was found to contribute significantly to the degree of dispersion and to skewness of elution curves.   Anomalous bimodal characteristics of the elution curves were also observed which could only be ascribed to the empty tubing.   These phenomena depended markedly on parameters such as tube diameter and length, and solute concentration and molecular weight.   Dispersion in the packed column, although important, was found to be symmetrical (Gaussian) and less sensitive to these parameters than in the empty tubing, especially with respect to molecular weight.   Dispersion in the cell was believed to be insignificant relative to the packed column and empty tubing.

EXPERIMENTAL

The experiments performed in this study were designed so as to confirm some of the theoretical predictions made in part I of this paper[1] concerning resolution dispersion in GPC.

Apparatus

The basic instrument used in this work was the Waters Associates gel permeation chromatograph Model 100, which had been modified in the following way to make its analytical capabilities equivalent to the Model 200:

1.   The electromechanical and optical systems in the Model 100 were replaced with the R-4 conversion kit.

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* Present address: General Electric Company, Pittsfield, Massachusetts.

2. The stainless-steel liquid-end Milton Roy pump was replaced with a sapphire, liquid-end Milton Roy minipump.

3. The standard Leeds-Northrup recorder was replaced with a high-speed Honeywell Electronic-19 recorder which allows variations in chart speed from 1 in./10 min to 1 in./20 sec and ten times the change in attenuation possible with the standard recorder.

4. The heat exchanger tubing in the refractometer block was eliminated by reversing the flow to the refractometer. In order to prevent air bubble formation in the cell and also to stabilize the recorder baseline, the outlet of the cell was raised 3 ft above the refractometer block. This modification permitted the use of as little as 18 in. of connecting tubing between the sample injection valve and the refractometer cell.

5. The sample injection system was modified so as to permit the introduction of a step input of solute. For these experiments the sample loop in the injection valve was replaced with longer tubing having a capacity of 6 cc of sample solution. This was estimated to be sufficient to permit dispersion experiments to be conducted in 1-mm diameter tubing (d_t) up to 141 in. in length.

6. To damp the effects of sudden pressure changes caused by opening and closing the sample injection valve, a column packed with glass beads was installed in the solvent line between the pump and the inlet to the sample valve.

Packed Column Preparation

Glass beads of approximately 50μ average diameter (d_p) were cleaned by steeping in toluene for at least three days with intermittent agitation. The beads were washed several times with toluene (C.P. grade) until the supernatant liquid had the same refractive index as the pure toluene. A slurry of the glass beads in toluene was then prepared and added dropwise to a stainless steel column with 0.307-in. diameter (d_T) and 4-ft length, identical to that supplied by Waters Associates. The slurry was added continuously with intermittent shaking (60-cycle vibrator) until the column was fully packed with no further observable settling of the beads. It was estimated that

$$\alpha \equiv \frac{V_0}{V_T} \approx 0.35$$

where V_0 is interstitial volume of the packed column = 20.5 cc, and V_T is total volume of the packed column = 58 cc.

Sample Preparation

Polystyrene standards with molecular weights of 900, 20,400, 51,000, 97,200, and 160,000 and dispersion index $\bar{M}_W/\bar{M}_N$ of approximately 1.06 (Pressure Chemical Company) were weighed on an analytical balance and diluted in a volumetric flask with toluene to solute injection concentrations

(C_0) of 0.3, 0.6, 1.5, and 6.0 g/l.   The solutions were subsequently agitated over a period of at least 3 hr to ensure complete dissolution of the polystyrene granules.

Measurements and Calculations

A volumetric flow rate u of 1 cc/min was used in all experiments.   Reynolds numbers were calculated to be approximately $Re_p = 0.05$ for the packed column and $Re = 30$ for the empty tubing.

Pertinent time parameters such as minimum residence time and sample injection time were carefully monitored with a stopwatch.   Minimum residence time was recorded as the time which elapsed between the instant the sample injection valve was opened to the instant the recorder pen responded. Sample injection time ϵ in experiments with rectangular pulse inputs was recorded as the time which elapsed between the opening and closing of the sample injection valve.   For the shortest tubing length (18 in.), ϵ was 5 sec and in all other experiments, 20 sec.

The effective volume V_e of the entire system was defined in general as

$$V_e = V_0 + V_t + V_c$$

because the column packing was nonporous;   here, V_t = volume of empty tubing (0.02 cc./in.) and V_c = volume of refractometer cell = 0.07 cc. It is obvious that V_e is related to the mean residence or retention time θ by $V_e = u\theta$.   Since V_c was small, in most experiments involving only empty tubing and no packed column, $V_e \approx V_t$; and, with a packed column, $V_e \approx V_0 + V_t$.   Thus, V_0 of the packed column (20.5 cc) was measured by assuming that V_e was equal to the value of the retention volume V_r at the peak of the elution curve ($c = c(V_r)$) of ODCB, which was the most Gaussian-like, corrected for the empty tubing volume V_t.   In this experiment the shortest length of tubing possible (23 in.) was used.

Since the values for ϵ were small compared with those for θ in all experiments involving rectangular pulse solute inputs, the elution curves were regarded as responses to delta function inputs whenever it was convenient to do so.   The validity of this approximation is guaranteed for Gaussian-like elution curves if the criterion[2]

$$\frac{V_s}{V_e\sqrt{n}} < 0.5$$

is satisfied, where $V_s \equiv u\epsilon$ is sample injection volume; $n = (\theta/\sigma)^2 = Pe_L/2$ is number of theoretical stages[1]; σ is standard deviation in units of time;   and $Pe_L \equiv L\bar{v}/D_L$ is dimensionless Peclet number.[1]

This inequality, which may be rewritten as

$$\frac{\epsilon\sigma}{\theta^2} < 0.5,$$

was satisfied in all experiments where it was convenient to consider the rectangular pulse as an impulse function.   For example, in the experiments

involving a packed column together with the shortest length of connecting tubing (23 in.), $\epsilon\sigma/\theta^2 = 0.0003$.

It was desirable to plot the elution curves $c = c(V_r)$ in dimensionless form. For pulse solute inputs

$$C^{**} = C^{**}(V_r{}^*)$$

and for step solute inputs

$$C^* = C^*(V_r{}^*)$$

where $V_r{}^* \equiv V_r/V_e$ is dimensionless retention volume; $C^* \equiv C/C_0$ is dimensionless solute concentration; $C^{**} \equiv CV_e/A$ is another dimensionless solute concentration; and A is weight of solute injected. It is clear that for rectangular pulse inputs

$$C^{**} = C^* \frac{V_e}{V_s} = C^*/V_s{}^*.$$

Dispersion variances, or standard deviations, expressed in units of volume ($\sigma_v{}^2$ and σ_v, respectively) in all experiments were obtained by numerical calculation of the moments of the elution curves (not normalized) for pulse solute inputs using the formula

$$\sigma_v{}^2 = \frac{\mu_2\mu_0 - \mu_1{}^2}{\mu_0{}^2}$$

where $\mu_0 \equiv \int c(V_r)dV_r$ is zeroth moment, μ_0 being proportional to A; $\mu_1 \equiv \int V_r C(V_r)dV_r$ is first moment; and $\mu_2 \equiv \int V_r{}^2 C(V_r)dV_r$ is second moment. These computations were made via the well-known Gaussian quadrature integration technique. All numerical computations in this study were performed on an IBM Model 360 digital computer using the S/360 CSMP program.

Variances or standard deviations of elution curves may be obtained by a much simpler method[3] which uses the distance W between the points of intersection of tangents to the inflection points and the baseline

$$\sigma_v = \frac{W}{4},$$

but this method is only valid for Gaussian-type elution curves. An equivalent, more convenient method[3] of computing σ_v which is often used for symmetrical or quasisymmetrical elution curves[4] involves the width of the elution peak at one-half its height, $W_{1/2}$, as follows:

$$\sigma_v = \frac{W_{1/2}}{2.36}.$$

It was found in this work, however, that for elution curves which were skewed and exhibited a small amount of "tailing," large errors resulted when either of these methods was used to compute σ_v.

RESULTS AND DISCUSSIONS

Responses to Pulse Inputs

The elution curves for rectangular pulse inputs of solute are presented in Figures 1 to 11 in dimensionless form. In all of these experiments it was necessary, of course, to include the refractometer cell since it is part of the
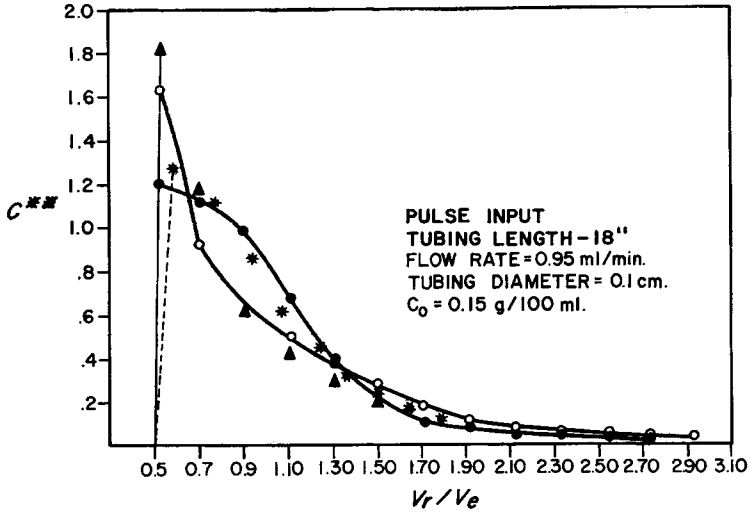

Fig. 1. Dimensionless response, C^{**} vs. $V_r{}^*$, to pulse input of solutes of various molecular weights for 18 in. of empty tubing: (●) ODCB; (O) PS-900; (▲) PS-20,400; (*) Computer model.
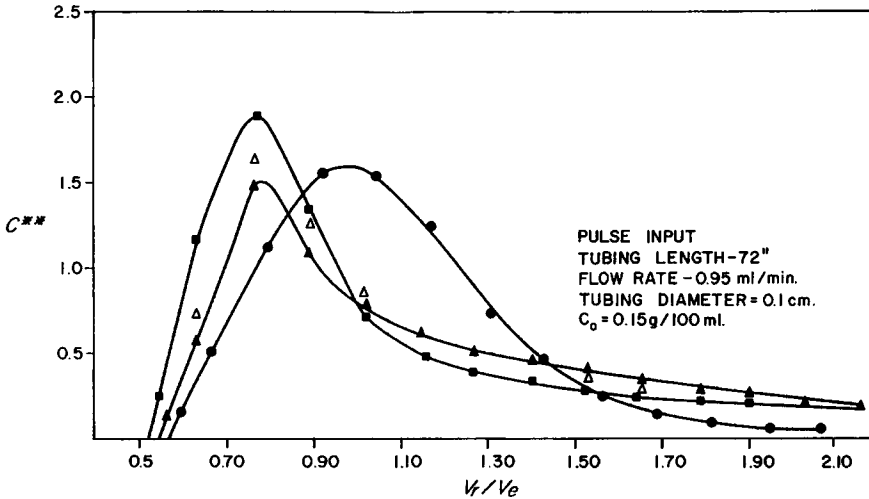

Fig. 2. Dimensionless response, C^{**} vs. $V_r{}^*$, to pulse input of solutes of various molecular weights for 72 in. of empty tubing: (●) ODCB; (▲) PS-20,400; (△) PS-97,200; (■) PS-160,000.
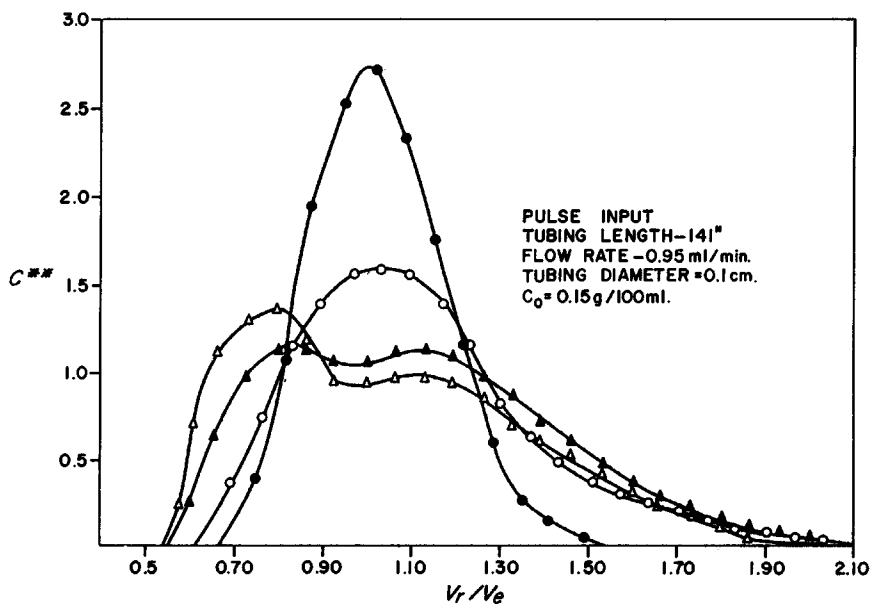
Fig. 3. Dimensionless response, C^{**} vs. $V_r{}^*$, to pulse input of solutes of various molecular weights for 141 in. of empty tubing: (●) ODCB; (○) PS-900; (▲) PS-20,400; (△) PS-97,200.
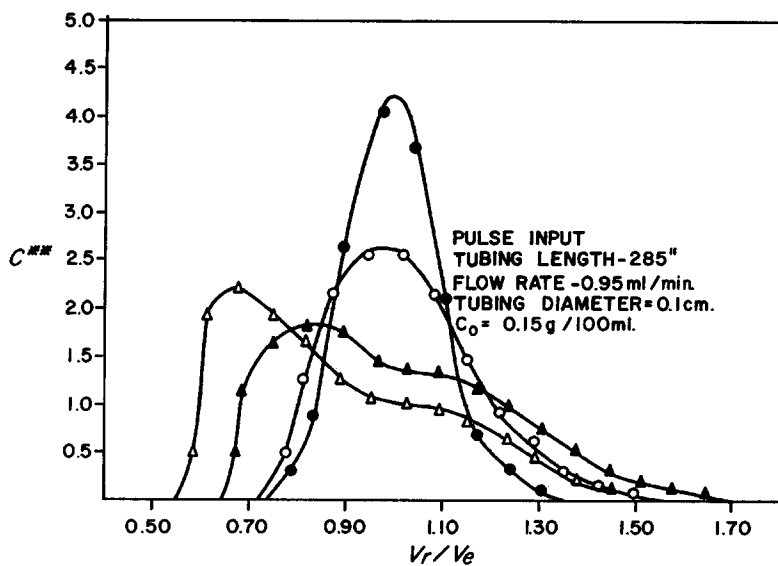

Fig. 4. Dimensionless response, C^{**} vs. $V_r{}^*$, to pulse input of solutes of various molecular weights for 285 in. of empty tubing: (●) ODCB; (○) PS-900; (▲) PS-20,400; (△) PS-97,200.
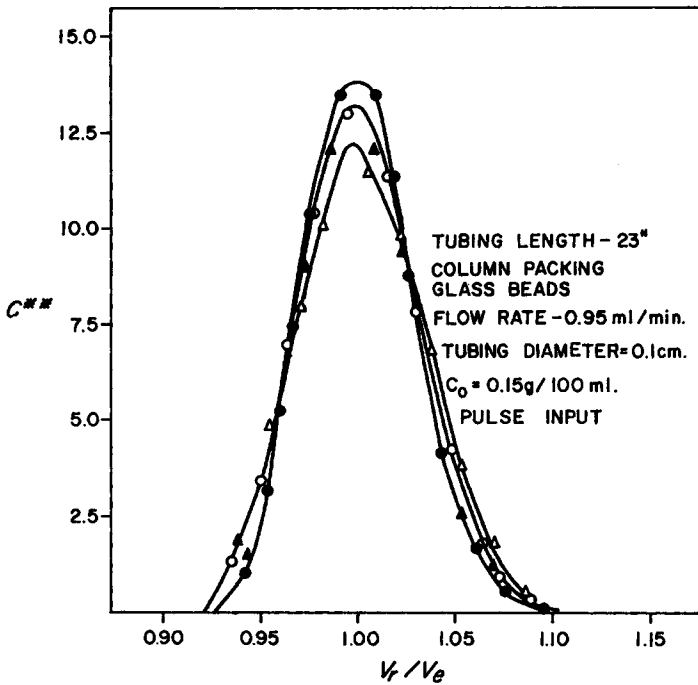
Fig. 5. Dimensionless response, C^{**} vs. V_r^*, to pulse input of solutes of various molecular weights for packed column–empty tubing (23 in.) combination: (●) ODCB; (○) PS-900; (▲) PS-20,400; (△) PS-97,200.

detection system. In Figures 1 to 4, the only other component present in the system was empty tubing (1 mm) of various lengths. In the remaining figures a single packed column with nonporous glass packing (50 μ) was included in addition to the various lengths of tubing. Initially the column was installed between the sample injection valve and the tubing (Figs. 5 to 8) and then between the tubing and refractometer cell (Figs. 9 to 11).

The mathematical model for dispersion due to segregated flow[1] in empty tubing is also shown in Figure 1 for comparison because the tubing length has its lowest value (18 in.) in this set of experiments and, therefore, the criteria for segregated flow are most likely to be satisfied, especially for large solute molecules (polymers). In fact

$$\frac{L}{\bar{v}} = 22 \quad \text{and} \quad \frac{R^2}{D} = 25 \times 10^3$$

if a value of 10^{-7} cm²/sec is assumed for the molecular diffusivity D of polystyrenes, which clearly shows that the criteria for segregated flow are satisfied. This mathematical model was computed by substituting eq. (10a) (of part I[1]) with

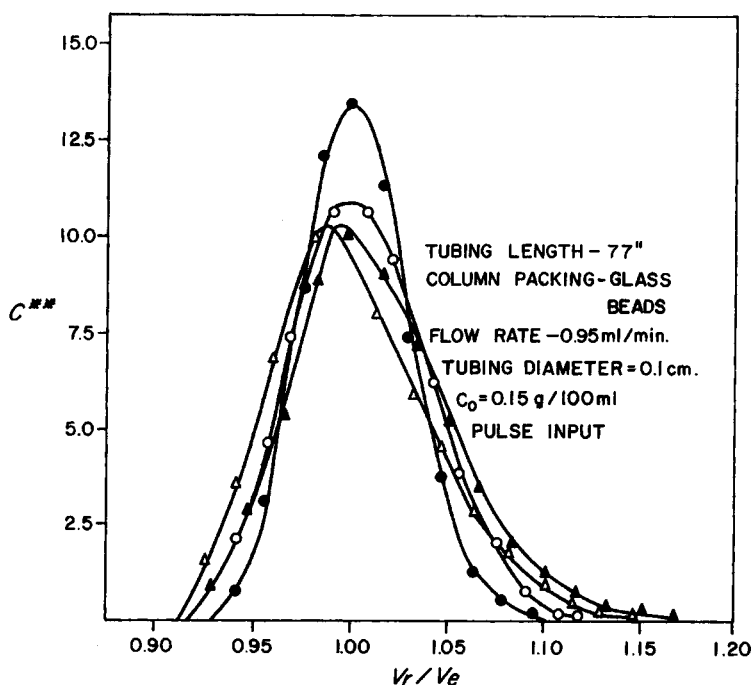$$\epsilon = 5 \text{ sec and } \theta = 0.43 \text{ min}$$

Fig. 6. Dimensionless response, C^{**} vs. V_r^*, to pulse input of solutes of various molecular weights for packed column–empty tubing (77 in.) combination: (●) ODCB; (○) PS-900; (▲) PS-20,400; (△) PS-97,200.

into eq. (4)[1] for C_e and solving the resulting equation numerically. Thus, dispersion in the refractometer cell, albeit small, was included. Although the agreement between the model and experiment is good, it appears to be somewhat better for small solute molecules (ODCB) than for large ones (polystyrenes). This result was not anticipated and was thought, at first, to be the result of errors in the measurements.

The dispersion model for the Taylor diffusion regime[1] is Gaussian. Hence, experimental elution curves for sufficiently long tubing such that criterion (12a) or (14) is satisfied should approach eq. (6).[1] As expected in this case the solute having the lowest molecular weight (ODCB) is most accurately described by this mathematical model (Figs. 1 to 4).

The anomalous bimodal characteristics of elution curves for long empty tubing and high molecular weight polymers (20400, and 97,200) which appear in Figures 3 and 4 were not anticipated from the theory although other workers[5,6] have alluded to similar findings. The cause of such anomalies has been attributed to the refractometer cell.[5] However, if this were true for the bimodal phenomenon observed in this work, then it would not depend on tubing length which, as inspection of Figures 1 to 4 shows, it clearly does. These figures also suggest a strong molecular weight dependence. It is possible that the unexpected deviation of the polymer elution
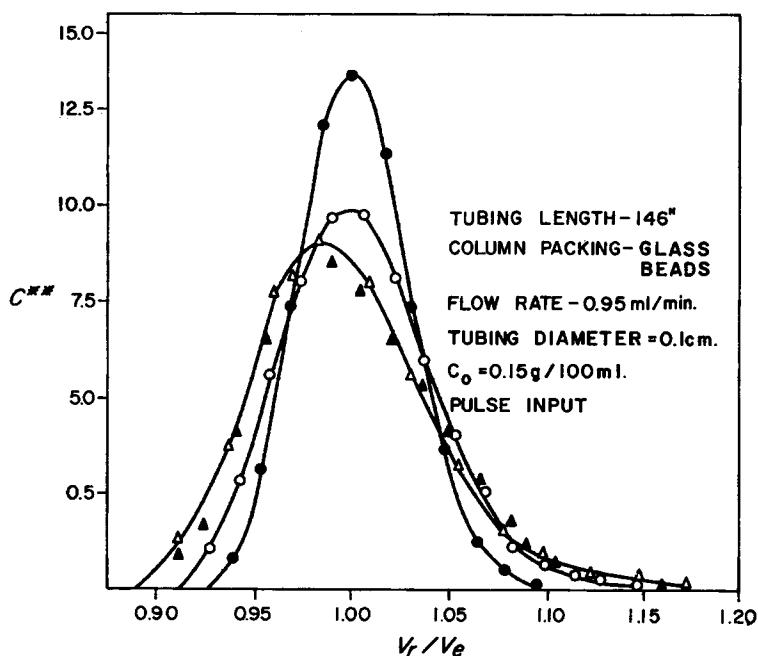
Fig. 7. Dimensionless response, C^{**} vs. V_r^*, to pulse input of solutes of various molecular weights for packed column–empty tubing (146 in.) combination: (●) ODCB; (○) PS-900; (▲) PS-20,400; (△) PS-97,200.

curves from the segregated flow model reflects the onset of the same phenomenon observed with longer tubing.

Further investigations into the causes of the anomalous elution curves are currently in progress. At present it is believed that such behavior is peculiar to flowing macromolecules in solution and involves intermolecular interactions or "entanglements" between polymer molecules, causing them to cluster into a plug near the tube axis.

In Figure 5 it is clearly seen that dispersion in the packed column dominates, since the empty tubing is short (23 in.), and is Gaussian-like and relatively independent of molecular weight as expected.[1] It is believed that the slight differences among the elution curves are due to the empty tubing which, although it is only 23 in. in length, is beginning to manifest its ability to contribute to dispersion. The effects of the tubing on dispersion are clearly observable in Figures 6 to 8 and 9 to 11. They obviously include a tendency to broaden the dispersion of the elution curves and to cause the curves to become skewed (non-Gaussian) by shifting the peaks to lower values of retention volume V_r and introducing a tail at high values of V_r. Only the elution curves of ODCB become more symmetrical with increasing tubing length (Figs. 8 and 11) as expected,[1] since they obey the same mathematical model, eq. (6),[1] in both the packed column and the empty tubing under the appropriate conditions, and this model is Gaussian.
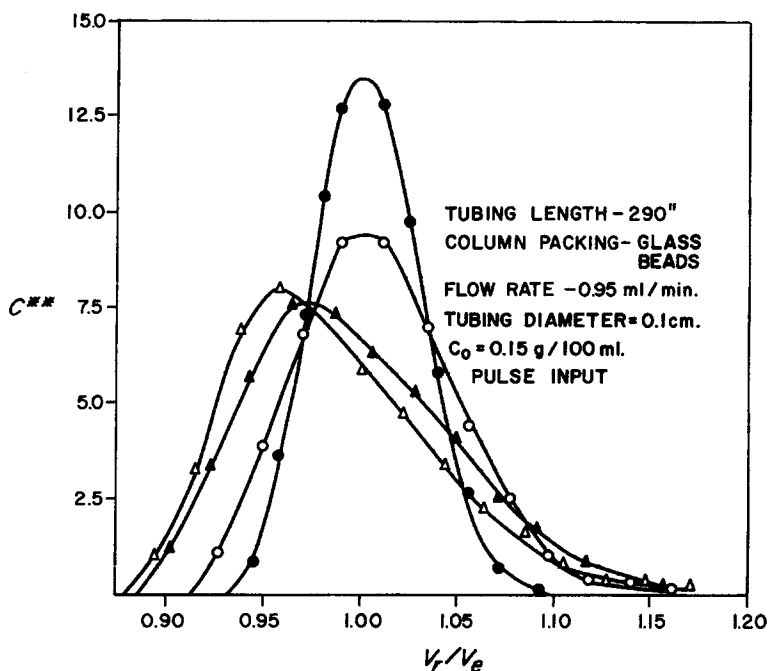
Fig. 8. Dimensionless response, C^{**} vs. $V_r{}^*$, to pulse input of solutes of various molecular weights for packed column–empty tubing (290 in.) combination: (●) ODCB; (O) PS-900; (▲) PS-20,400; (△) PS-97,200.

A comparison of Figures 6 to 8 with Figures 9 to 11 shows that the presence of empty tubing has a more pronounced effect on dispersion when connected before the column than after it. Even the anomalous bimodal characteristics of the empty tubing elution curves seem to be manifest in Figures 10 and 11.

Variances $\sigma_v{}^2$ and standard deviations σ_v for dispersion of different molecular weights in various lengths of tubing with and without the presence of a packed column, connected before and after the tubing, are pre-

TABLE I

Variance and Standard Deviation of Dispersion in Empty Tubing

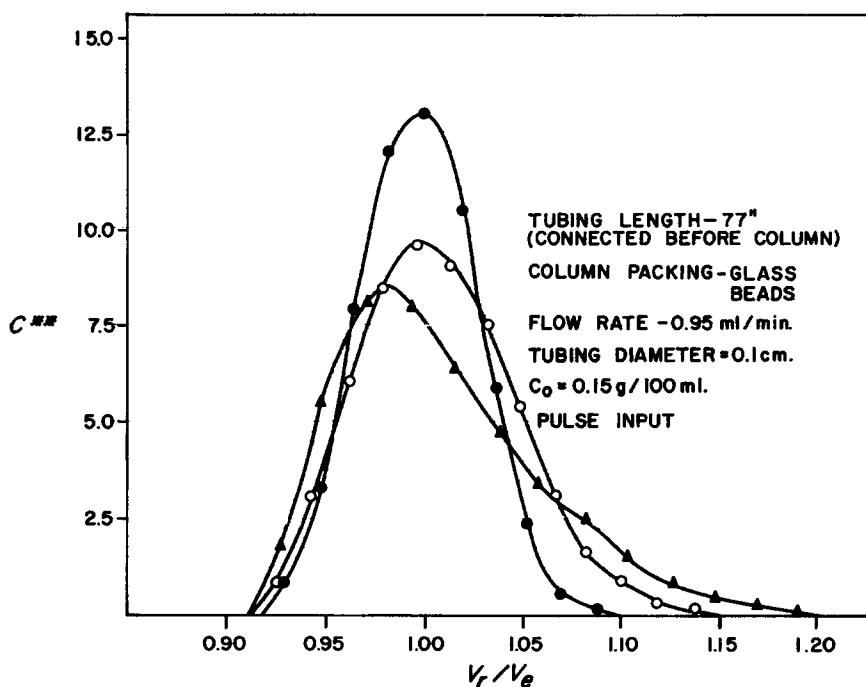|	$L = 18$ in.		$L = 72$ in.		$L = 141$ in.		$L = 285$ in.	
Solute	$\sigma_v{}^2$, cc^2	σ_v, cc	$\sigma_v{}^2$, cc^2	σ_v, cc	$\sigma_v{}^2$, cc^2	σ_v, cc	$\sigma_v{}^2$, cc^2	σ_v, cc
ODCB	0.042	0.204	0.18	0.424	0.18	0.424	0.29	0.538
PS-900	0.063	0.251	0.37	0.61	0.68	0.826	0.87	0.96
PS-20,400	0.048	0.219	0.66	0.812	0.88	0.938	1.46	1.209
PS-51,000	0.040	0.200	0.65	0.806	0.89	0.942	1.45	1.203
PS-97,200	0.032	0.179	0.57	0.755	1.14	1.068	2.13	1.460
PS-160,000			0.61	0.781	1.03	1.015	2.03	1.425

Fig. 9. Dimensionless response, C^{**} vs. V_r^*, to pulse input of solutes of various molecular weights for empty tubing (77 in.)-packed column combination: (●) ODCB; (○) PS-900; (▲) PS-20,400.

sented in Tables I and II. Examination of Table I shows that σ_v for ODCB is relatively insensitive to tubing length as compared with polystyrene and that the higher the molecular weight of the solute, the more sensitive is its σ_v to tubing length. This is in accord with theory,[1] which predicts that dispersion of ODCB, which has a larger molecular diffusivity ($D \sim 10^{-5}$ cm^2/sec) than polystyrene ($D \sim 10^{-7}$ cm^2/sec), should approach the Taylor regime more rapidly (at shorter tubing lengths) than polystyrene

TABLE II
Variance and Standard Deviation
of Dispersion in Packed Column and Empty Tubing

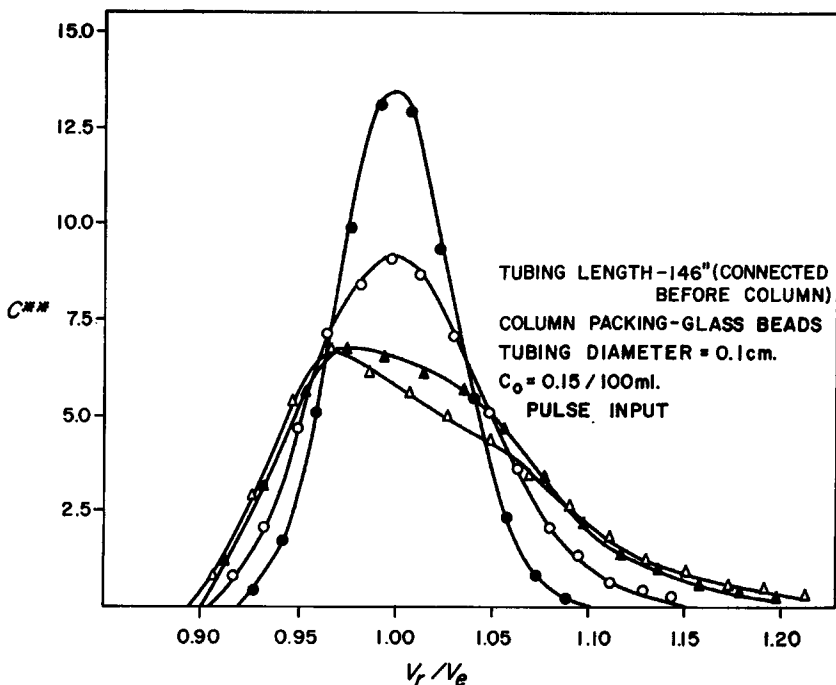| Solute	$L = 23$ in.		$L = 77$ in.		$L = 146$ in.		$L = 290$ in.	
	σ_v^2, cc^2	σ_v, cc	σ_v^2, cc^2	σ_v, cc	σ_v^2, cc^2	σ_v, cc	σ_v^2, cc^2	σ_v, cc
ODCB	0.23	0.48	0.40	0.63	0.41	0.64	0.48	0.69
PS-900	0.29	0.54	0.62	0.78	0.84	0.91	1.16	1.07
PS-20,400	0.30	0.55	0.88	0.93	0.93	0.96	1.80	1.34
PS-51,000	0.34	0.58	0.86	0.92	1.20	1.09	1.98	1.40
PS-97,200	0.41	0.64	0.97	0.98	1.46	1.21	2.39	1.54
PS-160,000			0.99	0.99	1.45	1.21	2.78	1.68

Fig. 10. Dimensionless response, C^{**} vs. V_r^*, to pulse input of solutes of various molecular weights for empty tubing (146 in.)–packed column combination: (●) ODCB; (O) PS-900; (▲) PS-20,400; (△) PS-97,200.

and that dispersion due to Taylor axial diffusion should increase with tubing length much more slowly than that due to the velocity gradient alone (segregated flow).

Moreover, theory predicts[1] that the standard deviation for the packed column alone should lie within the approximate range 0.1 cc. $< \sigma_v < 0.3$ cc. This prediction is based on values for Pe_L, $10^4 < Pe_L < 5 \times 10^4$, which follow from engineering correlations on packed columns and apply to columns with tubing length to particle diameter ratio and V_0 similar to those of the column used in the present experiments. A more recent correlation involving GPC columns[5] leads to a value of approximately 0.5 $\times$ 10^4 for Pe_L and thus 0.42 cc for σ_v.

It is possible to compare these predictions with experiment if it is assumed that the variances for the packed column and empty tubing are additive, which is strictly true only for Gaussian elution curves. The variances for the column may be obtained by subtracting the values in Table I, after correcting them for an additional 5 in. of tubing, from the corresponding values in Table II. Such calculations, many of which are certainly in error owing to the skewness introduced by the empty tubing, show surprisingly good agreement with theory although many values of σ_v are somewhat higher than predicted. However, the one which is probably the most

accurate, that for ODCB and the longest tubing, gives a value for σ_v of 0.33 cc, which is in excellent agreement with theory.

The relative importance of the contribution to total dispersion made by the empty tubing is apparent at tubing lengths of 72 in. or greater. For high molecular weight polystyrene, the dispersion variance of the 72-in. tubing was approximately equal to or even slightly greater than that of the column.
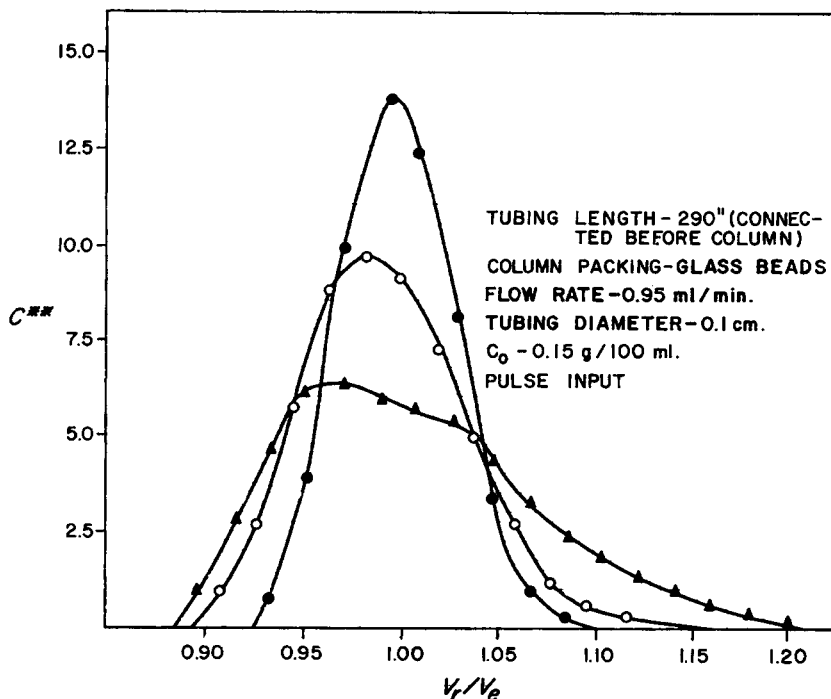

Fig. 11. Dimensionless response, C^{**} vs. V_r^*, to pulse input of solutes of various molecular weights for empty tubing (290 in.)–packed column combination: (●) ODCB; (○) PS-900; (▲) PS-20,400.

Assuming that the dispersion of ODCB in 285 in. of empty tubing was within the Taylor regime (Gaussian), the value of Pe_L was computed (Table I) from $\sigma_v = 0.538$ cc via eq. (7)[1] and found to be 225. From this it was estimated that the axial dispersion coefficient D_L had the remarkably high value of 6.7 cm²/sec. This is probably a fairly accurate estimate since it requires that the value of the molecular diffusivity D of ODCB in toluene be 3.4×10^{-5} cm²/sec., ((from equation (15)[1]) which is a reasonable value. Moreover, it is easy to show that

$$Pe \equiv \frac{L\bar{v}}{D} = 4.5 \times 10^7, \frac{L}{\bar{v}} = 345, \frac{R^2}{D} = 74,$$

and

$$\frac{2}{(3.8)} \, 2 \frac{R^2}{D} = 10,$$

which is consistent with the assumption that the criteria for Taylor diffusion[1] are satisfied.

Assuming that dispersion of ODCB in the packed column was Gaussian, a value for Pe_L of 7,600 was computed from eq. (7)[1] using $\sigma_\theta = 0.33$ cc, which is consistent with the assumption of Gaussian dispersion.[1] From this it was estimated that the axial dispersion coefficient D_L had a value of 1.6×10^{-3} cm²/sec. Although this value is in general agreement with that reported by other workers,[5] it is smaller by approximately three orders of magnitude than the dispersion coefficient for the empty tubing, even when the latter is in the Taylor regime, which itself represents a lower order of dispersion than that which is possible in empty tubing with high molecular weight solutes (segregated flow effect). It is appropriate at this point to observe that, whereas D_L in the packed column is proportional to $\bar{v}$, D_L in the empty tubing increases with $\bar{v}^2$ for Taylor diffusion.

Billmeyer and Kelley[5] have reported that the width of the elution peak of ODCB at half-height is greater than that of polystyrene. If this was to illustrate the difference in the magnitudes of dispersion, then their conclusion may be in error since an entirely different result is possible by using moments to estimate dispersion. Table I shows that for the shortest tubing length, the variances of ODCB and polystyrene are of the same order of magnitude.

Responses to Step Inputs

Step solute inputs were used in order to facilitate a comparison among the mathematical dispersion models for empty tubing, particularly in the region between the segregated flow and Taylor regimes where polymer solutions lie, and also to shed more light on the anomalous bimodal elution curves exhibited by these solutions at high molecular weight.

The responses to step inputs of solutes with various molecular weights in empty tubing of various lengths are plotted in dimensionless form in Figures 12 to 14. The segregated flow dispersion model is also plotted in each for comparison. This model was computed by replacing the integral in eq. (4)[1] with eq. (11a)[1] and solving the resulting differential equation numerically with the aid of a digital computer. Thus, dispersion in the refractometer cell was again included.

Since these curves are proportional to the integrals of the elution curves in Figures 1 to 3, the bimodal anomaly observed in the latter curved at high molecular weights and with long tubes appears as an inflection in the former. This inflection is apparent in Figure 14 for a tubing length of 141 in. and polymer molecular weights of 20,400 and higher. Although no inflection is visible in Figures 12 and 13, these curves do show a much sharper initial slope than the segregated flow model. This behavior is more characteristic
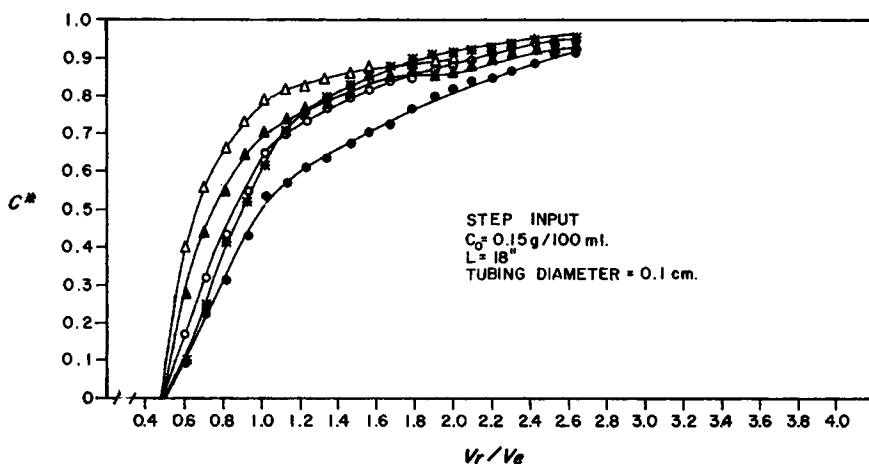
Fig. 12. Dimensionless response, C^* vs. V_r^*, to step input of solutes of various molecular weights for 18 in. of empty tubing: (●) ODCB; (○) PS-900; (▲) PS-20,400; (△) PS-97,200; (*) computer model.

Fig. 13. Dimensionless response, C^* vs. V_r^*, to step input of solutes of various molecular weights for 72 in. of empty tubing: (●) ODCB; (○) PS-900; (▲) PS-20,400; (△) PS-97,200; (*) computer model.

of "pseudoplastic" non-Newtonian flow than Newtonian flow, upon which the model is based.

The transformation of ODCB dispersion from the segregated flow regime toward the Taylor regime is apparent in Figures 15 to 17, which also show that the experimental data are accurately described by a mathematical dispersion model which is neither the segregated flow model nor the error function-type[1] for Taylor diffusion. This is a more precise model which was obtained by substituting the numerical solution (obtained from the
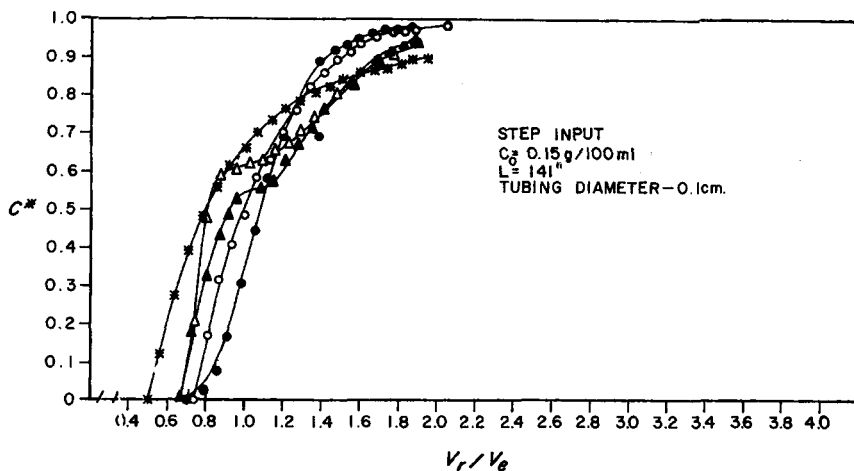
Fig. 14. Dimensionless response, C^* vs. V_r^*, to step input of solutes of various molecular weights for 141 in. of empty tubing: (●) ODCB; (○) PS-900; (▲) PS-20,400; (△) PS-97,200; (*) Computer model.
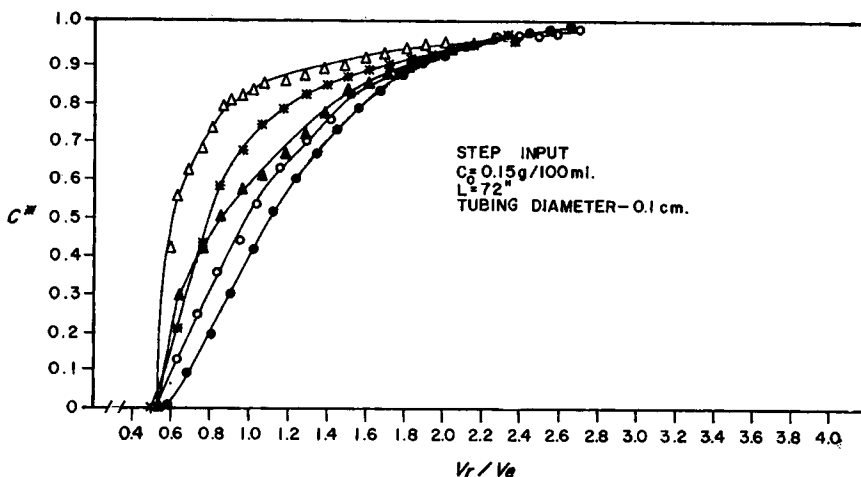

Fig. 15. Dimensionless responses, C^* vs. V_r^*, to step input of ODCB for 18 in. of empty tubing: (○) experimental; (●) theoretical, complete solution of dispersion equation; (*) theoretical, segregated flow model.

Library of Congress[7]) of the complete diffusion equation, eq. (3),[1] in place of the integral in eq. (4)[1] and solving the resulting equation with the aid of a digital computer. A good fit was accomplished by using a value for D (ODCB) of 1.5×10^{-5} cm²/sec, which is in general agreement with previous estimates. The effects of radial diffusion on the dispersion due to velocity gradients (segregated flow) are clear in Figures 15 to 17.
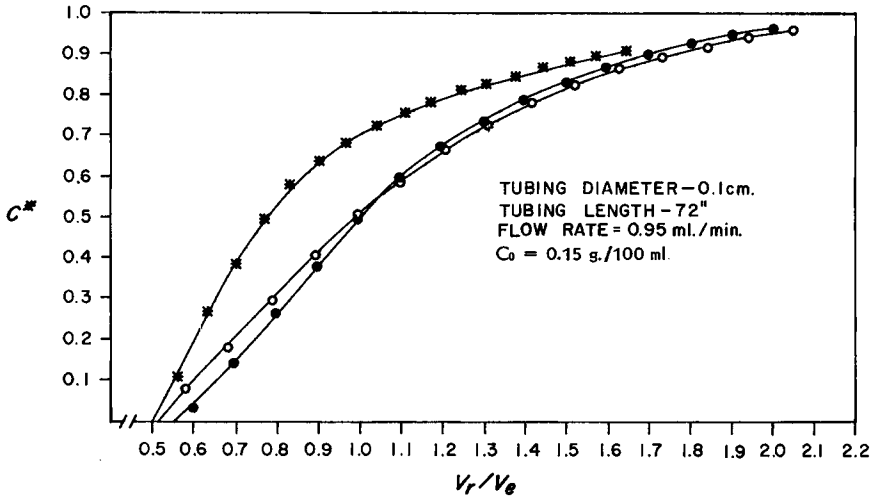
Fig. 16. Dimensionless responses, C^* vs. $V_r{}^*$, to step input of ODCB for 72 in. of empty tubing: (O) Experimental values; (●) Complete solution of the dispersion equation; (*) Segregated flow model.
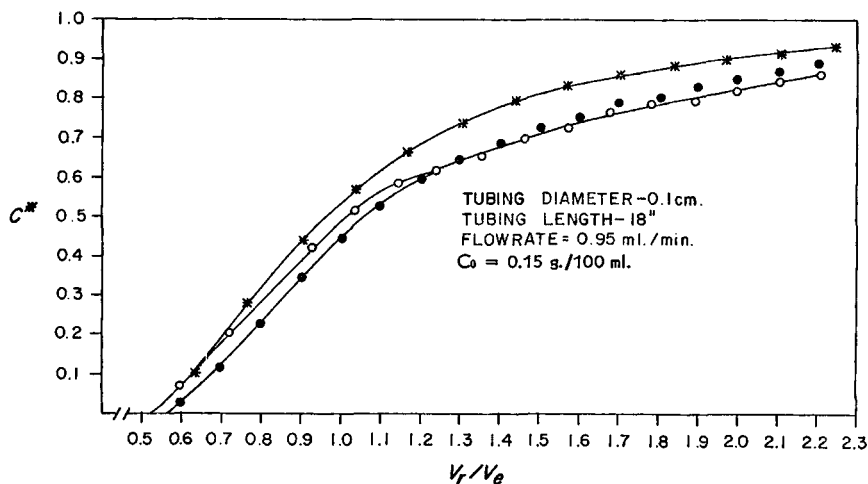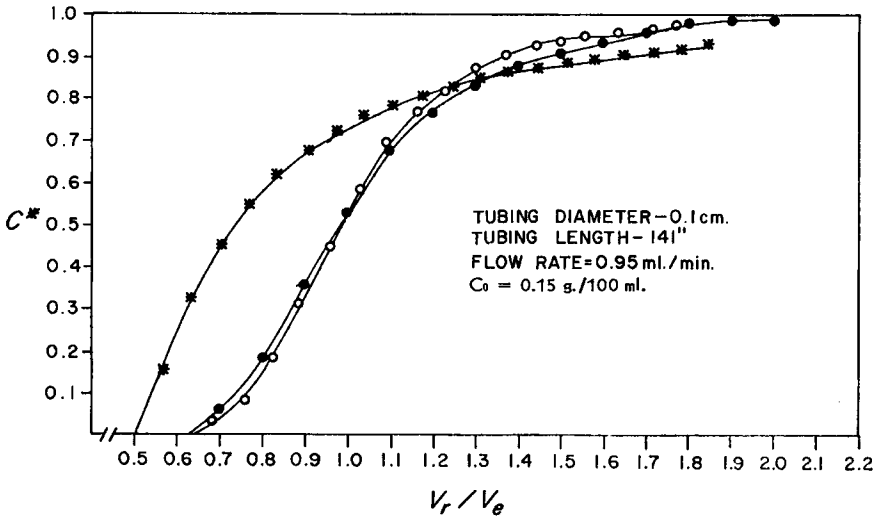

Fig. 17. Dimensionless responses, C^* vs. $V_r{}^*$, to step input of ODCB for 141 in. of empty tubing: (O) Experimental values; (●) Complete solution of the dispersion equation; (*) Segregated flow model.

Concentration Effects

Concentration of the polymer solute seems to have a profound influence on dispersion in the empty tubing. This is seen in Figures 18 and 19, which show the responses of 141 in. of empty tubing to step inputs of various concentrations of polymer solutes with molecular weights of 20,400 and 97,200. At high concentrations (6 g/l.), the response is pluglike and resem-
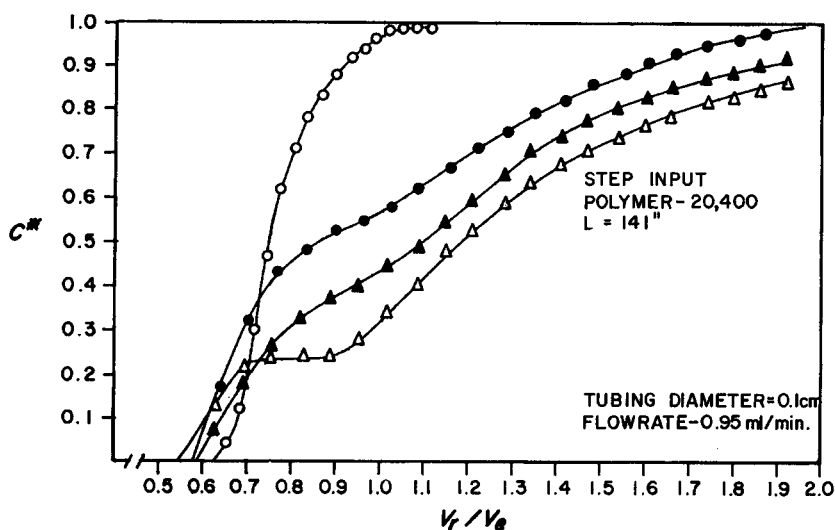
Fig. 18. Dimensionless response, C^* vs. V_r^*, to step input of polymer (PS-20,400) at various concentrations for empty tubing: (O) $C_0 = 0.60$ g/100 ml; (●) $C_0 = 0.15$ g/100 ml; (▲) $C_0 = 0.06$ g/100 ml; (△) $C_0 = 0.03$ g/100 ml.
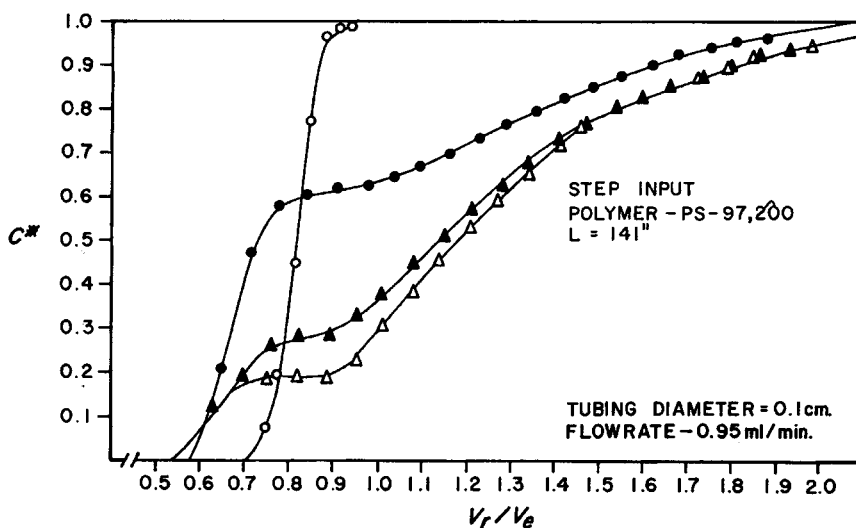
Fig. 19. Dimensionless response, C^* vs. V_r^*, to step input of polymer (PS-97,200) at various concentrations for empty tubing: (O) $C_0 = 0.60$ g/100 ml; (●) $C_0 = 0.15$ g/100 ml; (▲) $C_0 = 0.06$ g/100 ml; (△) $C_0 = 0.03$ g/100 ml.

bles a pseudoplastic fluid response more closely than that of a Newtonian fluid. This effect is reduced with dilution of the solute as the inflection becomes clearer and moves toward shorter retention times.

The non-Newtonian-like aspects of the responses are somewhat puzzling since polymer solutions with these concentrations and at these shear rates

are not generally expected to depart significantly from Newtonian behavior. It is possible to imagine this anomaly as being the result of polymer molecules in solution flowing through tubing more or less as a plug instead of moving at the streamline velocities.   Such behavior could be attributed to intermolecular "entanglement" which cause the macromolecular solute to cluster near the tube axis where shear rates and therefore shear stresses are the lowest.   Dilute slurries of pulp fibers have been observed[3] to exhibit such behavior.   Work is now in progress to investigate this anomaly further.

Effect of Tubing Diameter

If the diameter of the empty tubing is reduced by a factor of $^1/_2$ while other variables such as flow rate are maintained constant, the effect is to increase the shear rate by a factor of 8.   Furthermore, if it is assumed that the anomaly observed is the result of molecular interaction of the solute, then shear rate should have a pronounced effect on dispersion.

This effect was indeed found and is shown in Figure 20.   In these experiments the tubing lengths (141 and 512 in.) were adjusted subsequent to reducing the tubing diameter from 1 mm to 0.483 mm so as to maintain the residence time in the tubing constant.   The two solutes investigated were polystyrenes having molecular weights of 20,400 and 97,200.   The anomalous response was found to disappear for both solutes at high shear rates but the breakthrough values of elution volume, viz., those for streamlines at the tube axis, are all somewhat higher ($\sim$0.6) than expected ($\sim$0.5).

Another important observation at high shear rates is that the response appears to have less "tailing" than predicted by the segregated flow model;

Fig. 20. Dimensionless response, C^* vs. V_r^*, to step input of polymer (PS-97,200 and PS-20,400) for empty tubing of different diameters: ($\bullet$) D = 0.048 cm., PS 97,200; (O) D = 0.1 cm., PYS 97,200; ($\blacktriangle$) D = 0.048 cm., PS 204,000; ($\triangle$) D = 0.1 cm., PS 204,000.

i.e., the longest residence time in the experiments seems to be shorter than expected. Moreover, the responses are clearly less sensitive to molecular weight.

Finally, since the average shear rate in 0.4-mm tubing with a flow rate of 1 cc/min is of the order of 1,300 sec^{-1}, it is not unreasonable to consider also the possibility that radial migration of solute macromolecules toward the tube axis occurs and contributes to the anomaly. Suspended fibers in Poiseuille flow have been observed[9] to migrate toward the tube axis; other examples of similar radial migration phenomena have also been reported.[10-12]

SYMBOLS

L = length of column or tubing

R = radius of column or tubing

d_p = particle diameter of column packing

d_T = column diameter

d_t = diameter of tubing

V_r = ut = retenotin volume (variable)

V_0 = interstitial volume of the packed column

V_T = total volume of the packed column

V_t = volume of the empty tubing

V_C = volume of the refractometer cell

V_e = $V_0 + V_t + V_C$ = effective volume of the entire system

V_S = sample injection volume

V_r^* = V_r/V_e = dimensionless retention volume

V_S^* = V_S/V_e = dimensionless sample injection volume

α = V_0/V_T = interstitial volume fraction

ϵ = sample injection time

θ = mean residence time

θ_C = mean residence time in the refractometer cell

$\bar{v}$ = mean fluid velocity

u = volumetric flow rate

σ = standard deviation of elution curve in units of time

σ_V = standard deviation of elution curve in units of volume

C = solute concentration at any point

C_0 = solute concentration of sample injected

A = weight of solute injected

C^* = $C \left/ \dfrac{A}{V_s} \right.$ = C/C_0 = dimensionless concentration convenient for step solute injection

C^{**} = $C \left/ \dfrac{A}{V_e} \right.$ = CV_e/C_0V_s = dimensionless concentration convenient for pulse solute injection

D = molecular diffusivity of solute

D_L = axial dispersion coefficient in packed columns or tubing

ρ = density of solution

μ = viscosity of solution

R_e = $\dfrac{d_t \bar{v} \rho}{\mu}$ = Reynolds number used for tubing

Re_p = $\dfrac{d_p \bar{v} \rho}{\mu}$ = particle Reynolds number used for packed column

Pe = $\dfrac{L\bar{v}}{D}$ = Peclet number

Pe_L = $\dfrac{L\bar{v}}{D_L}$ = axial Peclet number

Pe_p = $\dfrac{d_p \bar{v}}{D_L}$ = particle Peclet number

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