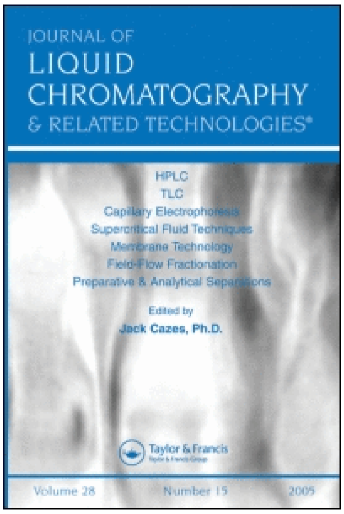

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Janĉa, Josef(1982) 'Concentration Dependence of Dispersion of Polymer Solutions Flowing in Capillaries', Journal of Liquid Chromatography & Related Technologies, 5: 9, 1621 — 1643
To link to this Article: DOI: 10.1080/01483918208067601
URL: http://dx.doi.org/10.1080/01483918208067601

JOURNAL OF LIQUID CHROMATOGRAPHY, 5(9), 1621-1643 (1982)

CONCENTRATION DEPENDENCE OF DISPERSION OF POLYMER SOLUTIONS FLOWING IN CAPILLARIES

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ABSTRACT

Dispersion of polymer solutions flowing in capillaries is an important phenomenon the knowledge of which is necessary for quantitative evaluation of polymer separations by chromatographic methods. The papers published in this field present a number of contradictory results. At various concentrations and various molecular weights also some other phenomena occur in the case of polymers, such as, e.g., non-Newtonian behaviour, which can affect dispersion.

In the present work influences of polymer molecular weight, specific viscosity of the polymer solution injected as a pulse or as a step into a capillary and influence of the flow-rate were studied. Experimental conditions were selected, so as to avoid possible interfering effects. The results confirmed our theoretical considerations and numerical calculations of other authors.

INTRODUCTION

The flow of polymer solutions in narrow capillaries also occurs in a number of natural and technological processes. Among them, chromatographic separation methods, such as, e.g., Steric-Exclusion

Chromatography (SEC), occupy an important place. The movement of the chromatographic zone through a random spatial porous structure of the column packing is a complicated process. In microscopic view, elementary transport phenomena occur in short pore segments between packing particles and are controlled by the same laws as the flow in the capillary. This is why the knowledge of elementary phenomena appearing during the flow of polymer solutions through narrow capillaries makes it possible to undersand also more complicated phenomena that occur in porous materials.

A number of authors have already studied dispersion of polymer solutions flowing in capillaries and its consequences for the separation by SEC method. Billmeyer and Kelley (1) observed considerable tailing in the chromatogram of a polystyrene (PS) solution. They did not notice this phenomenon with low-molecular weight solutes. They explained it by a worse mixing of PS solution which is more viscous. Besides this, they found some other anomalies, such as occurrence of negative peaks. These anomalous effects were suppressed by the use of a refractometric detector with a smaller volume of the measuring cell.

Biesenberger and Ouano (2) and Ouano and Biesenberger (3,4) carried out in detail both theoretical and experimental study on the dispersion of polymer solution in capillaries. The differential mass balance describing the dispersion of the solute was the starting point for their theoretical study

$$\frac{\delta c}{\delta t} = - v \frac{\delta c}{\delta z} + D_R \frac{1}{r} \frac{\delta}{\delta r} \left(r \frac{\delta c}{\delta r} \right) + D_L \frac{\delta^2 c}{\delta z^2} \qquad (1)$$

c is the concentration of the solute, z is the longitudinal coordinate, t is the time, v is the velocity of the mobile phase, D_R and D_L are the coefficients of the radial and longitudinal diffusion, respectively. Solving this equation under the given boundary conditions, they obtained the functions describing the shape of the chromatographic zone under various flow conditions. Namely for the case of segregated flow regime, when the influences of both axial and radial diffusion are very weak with respect to low diffusion coefficients (as with macromolecules) or with respect to the characteristics of the capillary (short length of the capillary, L, or large r for the given mean linear velocity, $\bar{v}$) and for the case of Taylor´s regime, when $r \ll L$ and D is great and hence only the influence of axial diffusion is negligible. However, the experimental results were not in accord with theoretical considerations. The chromatograms showed anomalous shape, they were bimodal. These anomalies were the more marked the longer was the capillary length and the higher was the molecular weight of the used model PS standard.

Hess and Tierney (5) published a very important paper in which they treated solution of eqn. (1) numerically in connection with the study of the dispersion during the flow of a solution of macromolecules in a capillary. One of the important findings of their study is that the flattening of the velocity profile occurs which is the more marked the higher is the molecular weight of the polymer or the higher is the viscosity of its solution. Another important factor, discussed in their paper, is the influence of possible non-Newtonian behaviour of the polymer solution in consequence of which the velocity profile will also be flattened. Hess and Tierney stated that their numerical results indicate lower decrease in the dispersion than the one that was observed experimentally by other authors mentioned above.

In their subsequent work, Ouano and Biesenberger (6) substantially confirmed their earlier experimental findings by repeated experiments of their preceding works, however with the use of dual detection (a UV detector and a differential refractometer in series), i.e., under the conditions where it was possible to exclude assumed artefacts.

Mayock and coworkers (7), as well as Golay and Atwood (8), dealt with the problems of the dispersion in the capillary in the initial stages of the flow. They found out by numerical methods applied to the solution of eqn. (1) that in these initial stages, i.e., in the transient range between the segregated flow regime and Taylor´s flow regime, bimodal concentration profiles or bimodal elution curves may occur.

On the basis of the published experimental data and in the absence of physically clear theory on the molecular level, which would describe quantitatively various phenomena occurring in the discussed transport processes, neither the possibility can be excluded that, in the case of soluble polymers, the same phenomena occur as those observed by Daily and Bugliarello (9) for the flow of particles. These authors observed the tendency of dilute fibre suspensions to concentrate during the flow in the centre of the capillary and to establish conditions for non-Newtonian behaviour by their orientation in the flow. Similar observations were made by Goldsmith and Mason (10, 11).

In the present paper experimental study of the dispersion of polymer solutions during the flow in the capillary was extended with the aim of approaching a capillary model to real flow conditions in the chromatographic column so that these results might be used in future works to explain dispersion phenomena in SEC of polymers. Concentration dependence of the dispersion of polymer solutions flowing in the capillary is studied for the reason that considerable concentration gradients exist in the chromatographic column which result in viscosity gradients making appreciable contributions to the total zone broadening. Furthermore, the viscosity phenomena show considerable influence on the polymer separation by SEC, and from this point of view have already been evaluated in a number of papers (for review see ref. 12). Explanation of their nature will require additional studies.

EXPERIMENTAL

A very simple equipment was used for the measurements. A constant flow-rate of the solvent was effectuated by means of a home-made syringe pump. Solutions were injected with a six-port valve (Waters Assoc., Milford, Mass., U.S.A.). Stainless-steel capillaries (Knauer, Oberursel, FGR), of various lengths, 1 mm in the inside diameter, were used. The eluate was detected with a differential refractometer, model 2025/50 (Knauer, Oberursel, FGR) with the cell volume of 8 μl in the case of the pulse injection experiment and with an UV detector at the wavelength of 254 nm (Development Works, Czech. Acad. of Sci., Prague, Czech.) in the case of step injection experiment. The UV detector was modified so that the measuring cell was composed of a quartz capillary with the inside diameter of 1 mm, to which the stainless-steel capillary was directly connected. UV radiation passed perpendicularly to this cell, the effective volume of which was 8 μl. By this manner the flow disturbance on the passage from the stainless-steel capillary to the measuring cell of the detector was excluded. For registration a Linear recorder, model 355 (Linear Instruments Corp., Irvine, Ca., U.S.A.), was applied. The measurement of the elution volume was derived from the movement of mechanical parts of the pump and thereby it was fairly precise. Elution volumes were recorded in various volumetric intervals - counts - the volume of which was 2.5×10^{-2}ml in the case of the step injection and 2.0×10^{-1} ml in the case of the pulse injection. The injected volume was 30 μl in the case of pulse injection. In the step injection experiment, the injection loop was replaced with a capillary, 1 mm in the inside diameter and 5 m in the total length, being equal in the length to the capillary in which dispersion measurement was performed. With the pulse injection, the length of the used stainless-steel capillary was 248 cm. Toluene and tetrahydrofuran (THF) were used as solvents for the pulse injection and the step injection experiments, respectively. Toluene of analytical grade (Lachema, Brno, Czechoslovakia) was used directly, THF was distilled from cuprous chloride and potassium hydroxide in nitrogen atmosphere.

Solutions of naphthalene in toluene and polystyrene (PS) standards in toluene were injected in the pulse injection experiment and solutions of benzene in THF and PS standard in THF in the step injection experiment. Molecular weights of the used PS standards (Waters Assoc., Milford, Mass.,U.S.A.) are listed in Table 1.

The stainless-steel capillaries in which the experiments were performed were straight, without any coiling. They were inserted into a rubber tubing 1 cm in the inside diameter, in such a way that these capillaries passed through the perforated wall of the rubber tubing closely behind the injection valve and

TABLE 1

Molecular Weights of PS Standards Used for the Study (Manufacturer´s Data)

Standard	Molecular Weight
PS 1	2 700 000
PS 2	2 610 000
PS 3	867 000
PS 4	670 000
PS 5	470 000

just before the detector. Water, thermostated to the temperature of 25 ± 0.05 °C, circulated in the tubing. Thereby it was secured that the conditions of the experiment were precisely defined, constant and without any influences disturbing the hydrodynamic flow.

RESULTS AND DISCUSSION

The authors of the referred works (2-4, 6) performed their measurements in capillaries, 1 mm in the inside diameter, under the flow-rates used in practical SEC separations of polymers, i.e., 1 ml/min. This flow-rate corresponds to the linear velocity of the displacement of approximately 2 cm/sec. Columns for SEC are usually 4-8 mm in diameters and have the interstitial porosity $\emptyset = 0.35 - 0.40$. It follows from these data that linear velocities of the displacement in the interstitial volume are 5 to 25 times less under common chromatographic conditions than in the referred papers. In order to approach the conditions of linear velocities of the displacement in the column in this respect, when using the capillary with the inside diameter of 1 mm, we must operate within approximate range of the flow-rates of 0.04 - 0.20 ml/min. This is why we carried out our measurements at the two different flow-rates, 0.038 ml/min and 0.334 ml/min.

For the evaluation of the dispersion regime under the present experimental conditions, Peclet´s number, Pe,

$$Pe = L\,\bar{v} / D \tag{2}$$

and Taylor´s number (2), Ta,

$$Ta = R^2\,\bar{v} / LD \tag{3}$$

were used, where R is the radius of the capillary. For the given experimental conditions (particularly L and $\bar{v}$) Pe is always $Pe \gg 1$, which means that the contribution of the longitudinal diffusion is small. At the higher of the both studied flow-rates $Ta \gg 1$ for polymer solutions which means that segregated flow regime (2) is concerned, in which the radial diffusion is small. At the lower flow-rate $Ta > 1$ (approximately $Ta \doteq 8$), which means that rather a transient range between the segregated flow and Taylor regimes (2) is concerned. For low-molecular weight solutes (naphthalene, benzene) $Ta \ll 1$, with respect to a higher diffusion coefficient, i.e., at both of the flow-rates the condition of Taylor flow regime holds true.

In order to evaluate experimental data quantitatively from the viewpoint of the agreement or discrepancies between them and the theoretically assumed model of the flow regime, statistical moments of elution curves, μ_1' (the first statistical moment with respect to zero) and μ_n (the n-th central moment), defined by the equations

$$\mu'_1 = \Sigma V_i \, h_i \, / \, \Sigma h_i \tag{4}$$

$$\mu_n = \Sigma (V_i - \mu'_1)^n \cdot h_i \, / \, \Sigma h_i \qquad n=2,3,\ldots \tag{5}$$

were used, where V_i is the elution volume, h_i is the height of the chromatogram from the base-line. With the aid of Eqns. (4) and (5) it was possible to calculate the corresponding statistical moments of the elution chromatograms resulting from the pulse injection experiment. The statistical moments of the frontal chromatograms obtained by the step injection were calculated with the use of Eqns. (6) and (7)

$$\mu'_1 = \Sigma V_i \cdot (h_i - h_{i-1}) \, / \, H \tag{6}$$

$$\mu_n = \Sigma (V_i - \mu'_1)^n \cdot (h_i - h_{i-1}) \, / \, H \tag{7}$$

where H is the total height of the frontal chromatogram from the base-line up to the plateau for which it holds true that

$$H = \Sigma (h_i - h_{i-1}) \tag{8}$$

Based on these statistical moments, the criterion of elution curve asymmetry, A, was defined in the preceding work (13)

$$A = \mu_3 \, / \, (\mu'_1)^3 \tag{9}$$

Additionally, for the case of the dispersion which can be described by Eqn. (1), the relationship (14) between the number of theoretical plates, N, of the given system

$$N = (\mu_1')^2 / \mu_2 \tag{10}$$

and the asymmetry, A,

$$A = 4\ N^{-2} \tag{11}$$

was derived.

The agreement between the values of A_{exp}, calculated from the experimental chromatograms with the use of Eqn. (9), and theoretical ones, A_{theor}, calculated with the aid of Eqn. (11) for the values of N found experimentally (Eqn. (10)), can then serve as a suitable criterion for the evaluation of the accord between the theoretical assumption of the dispersion and the real experimental observations. In other words, the differences between A_{exp} and A_{theor} indicate that the real character of the dispersion differs from the one that is assumed by the used theoretical model. The above interpretation was used to evaluate both the pulse and the step injection experiments.

For the height equivalent to a theoretical plate, HETP, the known relationship can be written

$$HETP = L\ /\ N \tag{12}$$

For a circular capillary it then holds (15)

$$HETP = \bar{v}\ R^2\ /\ 24\ D \tag{13}$$

Eqn. (13) results from the solution of Eqn. (1) under the pertaining boundary conditions with axial diffusion being neglected and with the assumption of a parabolic velocity profile (16).

Diffusion coefficient is a function of dimensions or molecular weight of the solute molecules and the viscosity of the medium according to Stokes-Einstein equation

$$D = R^{\bullet} T / 6 \pi r_1 \eta N_A \qquad (14)$$

where $R^{\bullet}$ is the gas constant, T absolute temperature, r_1 the radius of the solute molecule, η viscosity of the medium and N_A Avogadro number. If a spherical solute macromolecule and a direct proportion between the volume of the macromolecule and its molecular weight can be assumed, Stokes-Einstein equation can be written in a more general form

$$D = \text{const} . 1 / (\eta M^{1/3}) \qquad (15)$$

Some empirical expressions describe the relationship between D and M increased to a higher power (up to $M^{2/3}$), such as, e.g., Wilke/Chang equation (17). The above relationships and equations became the basis for the quantitative evaluation of the experimental results.

Results of both pulse and step injection experiments, obtained at the two different flow-rates for a series of samples of PS standards having the given initial value of the specific viscosity, η_{spec} are listed in Tables 2-5. These specific viscosities of the injected solutions of PS standards were calculated from the known concentration of the solutions of PS standards of the given molecular weights with the use of the Mark-Houwink equations

$$[\eta] = 8.81 . 10^{-3} M^{0.75} \qquad (16)$$

valid for PS in toluene at 25 °C (18) and

TABLE 2

Results of the Pulse Injection Experiment Measured at a Flow-Rate of 0.038 ml/min

Sample	η_{spec}	μ_1'	μ_2	μ_3	N	A_{exp}	A_{theor}
Naphthalene 0.0625-4%	—	10.84	0.267	0.02	440	0.000016	0.000021
PS 1	9.458	15.94	20.82	67.95	12.2	0.0168	0.0269
	3.366	14.11	17.80	30.50	11.2	0.0109	0.0320
	1.342	12.38	11.45	21.69	13.4	0.0114	0.0223
PS 3	3.366	13.46	10.20	27.29	17.8	0.0112	0.0127
	1.342	11.24	8.85	21.11	14.3	0.0149	0.0196
	0.586	12.56	9.57	25.04	16.5	0.0126	0.0147
PS 5	3.366	12.11	5.13	9.92	28.6	0.0056	0.0049
	1.342	12.09	6.27	15.09	23.3	0.0085	0.0074
	0.586	11.92	6.37	15.26	22.3	0.0090	0.0080
	0.272	11.48	5.63	7.22	23.4	0.0048	0.0073

$$[\eta] = 1.17 \cdot 10^{-2} M^{0.717} \tag{17}$$

valid for PS in THF at 25 ^{o}C (19) and with the use of the Huggins equation

$$\eta_{spec} = [\eta] c + k_H [\eta]^2 c^2 \tag{18}$$

c in the above equations is concentration, $[\eta]$ is the intrinsic viscosity, M is the molecular weight and

TABLE 3

Results of the Pulse Injection Experiment Measured at a Flow-Rate of 0.334 ml/min

Sample	η_{spec}	$/u'_1$	$/u_2$	$/u_3$	N	A_{exp}	A_{theor}
Naphthalene 0.0625-4%	—	10.92	1.49	0.38	80.0	0.00029	0.00062
PS 2	9.458	25.71	107.5	882.6	6.1	0.0519	0.1058
	3.366	17.95	57.11	288.5	5.6	0.0499	0.1257
	1.342	14.50	23.60	25.5	10.6	0.0177	0.0358
PS 3	3.366	19.00	48.94	271.0	7.4	0.0395	0.0735
	1.342	14.90	25.36	100.8	8.8	0.0305	0.0522
	0.586	13.76	24.97	97.9	7.6	0.0376	0.0696
PS 5	3.366	16.67	25.19	71.2	11.0	0.0154	0.0329
	1.342	14.08	18.74	64.4	10.6	0.0231	0.0357
	0.586	11.40	8.12	17.8	16.0	0.0120	0.0156

the Huggins constant, $k_H = 0.362$, was measured in our previous work (20) for THF; for toluene it is $k_H = 0.34$ (18).

Let us notice now in detail the results summarized in Tables 2 and 3, i.e., the dispersion in the elution mode in the pulse injection. At the both, higher and lower flow-rates a marked dependence of $/u'_1$, i.e., of the average elution volume, on η_{spec} of the injected polymer solution was found. For better illustration it is shown in Fig. 1. This dependence

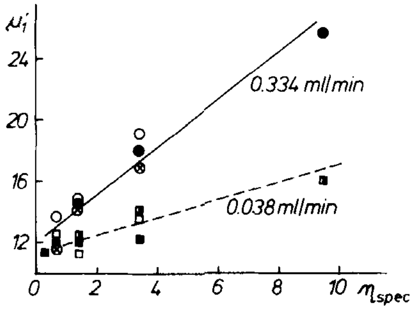

FIGURE 1
Dependence of the average elution volume on the specific viscosity of solutions of various PS standards injected as pulses.
Flow-rate: 0.334 ml/min: ● PS 2, ○ PS 3, ⊗ PS 5
Flow-rate: 0.038 ml/min: ◧ PS 1, □ PS 3, ⊠ PS 5

is only slightly influenced by the molecular weight of the solute. So far similar observation is concerned as with packed columns (21). In contradiction to the experiments with packed columns the dependence of μ_1' on η_{spec} is markedly less steep at the lower flow-rate. In order to demonstrate illustratively circumstances of the dependence of μ_1' on η_{spec}, Fig. 2 shows the chromatograms obtained by the injection of solutions of PS standards at different concentrations and thus at different values of η_{spec} at the higher flow-rate. The identical feature of a similar figure in our earlier work (21) is the fact that the frontal part of the chromatogram has almost identical course and origin for all of the three injections, whereas the back part is retarded more significantly as η_{spec} increases. Thereby the width of the chromatographic zone extends and tailing apparently increases. The values of A in

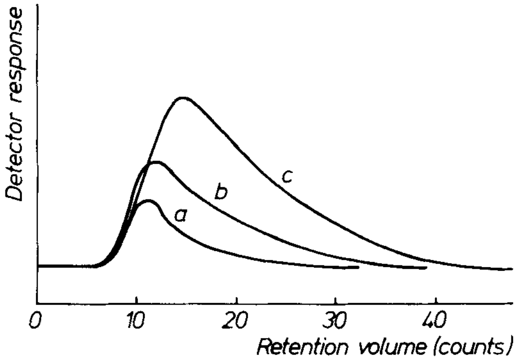

FIGURE 2
Chromatograms of PS 3 standard injected as a pulse at various concentrations at a flow-rate of 0.334 ml/min. a... $\eta_{spec} = 0.586$, b... $\eta_{spec} = 1.342$, c... $\eta_{spec} = 3.366$

Tables 2 and 3, however, show (again with a certain experimental variance) practical independence on η_{spec}. Thus an enlarged tailing declared by the authors of (2) is only apparent as it is a simple consequence of the increase in the zone width, characterized by μ_2 with an increasing η_{spec}. This dependence of μ_2 on η_{spec} is also entirely obvious in Tables 2 and 3 in spite of the variance of the experimental results being greater in consequence of experimental inaccuracies increased to the second power (see definition Eqn. (5)).

At the higher of the both investigated flow-rates the ratio A_{theor}/A_{exp} is approximately 2.0 for all of the injected PS standards and concentrations, with non-systematic variations in the range from 1.3 to 2.5. Even for naphthalene injected in a wide range of concentrations the ratio $A_{theor}/A_{exp} = 2$. The explanation obviously follows from the fact that although the injected volume is about 1.5 % of the total volume of the capillary, it is not infinitely small as it would be necessary for the ideal case, which causes the observed differences between A_{theor} and A_{exp}.

At the lower flow-rate the observed ratios A_{theor}/A_{exp} are lower; on average $A_{theor}/A_{exp} = 1.4$. The contribution to the broadening caused by the injection is doubtlessly less significant, regardless the fact that, with the exception of PS 1 standard, the other differences are assentially within the framework of experimental errors. It is obvious from Eqn. (11) that the error of 5 % in the reading of N will result in the error of about 10 % in the value of A.

With regard to Eqns. (10), (12), (13) and (15) it must hold true for the given constant viscosity of various injected PS standards

$$\frac{(/u_2)_{M_1}}{(/u_2)_{M_2}} = \left(\frac{M_1}{M_2}\right)^{1/3} \qquad (19)$$

and for the injection of PS standards of the given molecular weights and viscosities it then holds

$$\frac{(/u_2)_{\eta_1}}{(/u_2)_{\eta_2}} = \frac{\eta_1}{\eta_2} = \eta_{rel} = \eta_{spec} - 1 \qquad (20)$$

In consideration of the dilution of the polymer solution due to the zone broadening in the course of its movement along the column, all of the viscosities in Eqn. (20) have the meaning of average values which, however, are proportional to the values of viscosities of the injected solutions and therefore the latter ones can be used for the correlation.

The results presented in Table 2 and 3 show (with the variance given by experimental errors) basic agreement of experimental data with Eqns. (19) and (20). It means that in the case when diffusion takes place in a high degree (in the first place radial diffusion) the dependence of μ_2 on η_{spec} is primary. The dependence of μ_1' on η_{spec} is, in this case, only a consequence of the preceding dependence. The correlation of μ_2 values measured at various flow-rates with Eqn. (13) shows a good agreement between the theoretical assumption and the experiment for the low-molecular weight solute - naphthalene. An increase in HETP values of polymer solutions at the higher flow-rate is, however, substantially less than it corresponds to Eqn. (13). These facts, in the same way as the character of the chromatographic curves in Fig. 2, confirm that, at least at the higher of the both studied flow-rates, segregated flow regime takes place in the first place in consequence of which convective character of diffusion predominates. However, it is obvious that other phenomena of hydrodynamic character, such as establishment of other than parabolic velocity profile during the flow of polymer in the capillary, can take place.

The results of the step injection experiment are presented in Tables 4 and 5, again for the two above mentioned flow-rates. Sign "plus" in column "Specific Viscosity Step" indicates that the solution of PS 4 standard was injected into THF, the change in η_{spec} was thus positive and, reversely sign "minus", means that THF was injected into the solution of PS standard.

At the lower flow-rate, an inexpressive tendency to an average higher elution volume μ_1' can be observed if the solution of PS standard is injected into THF when

TABLE 4

Results of the Step Injection Experiment Measured at a Flow-Rate of 0.038 ml/min

Specific Viscosity Step	μ_1'	μ_2	μ_3	N	A_{exp} $.10^{-3}$	A_{theor} $.10^{-3}$
Benzene into THF	151.5	12.59	4.402	1823	0.0013	0.0012
+0.392	152.0	290.1	4847	79.6	1.38	0.63
+0.872	154.1	285.0	4227	83.3	1.16	0.58
+2.133	150.4	289.6	5266	78.1	1.55	0.66
-0.239	146.0	315.7	3226	67.5	1.04	0.88
-0.514	144.5	309.4	4336	67.5	1.44	0.88
-1.170	150.5	357.0	7029	63.4	2.06	0.99

compared with μ_1' of benzene injected into THF and the tendency to an average lower μ_1' with the injection of THF into the solution of the PS standard. This may be an indication of the establishment of the plug velocity profile with the injection of PS solution into THF on the zone boundary and "break-through" of the zone boundary by the less viscous THF on its injection into the PS solution, leading to the velocity profile elongated more than the parabolic one. Flattening of the velocity profile may be caused on the one hand by non-Newtonian behaviour of the polymer solution, which, however, appears more marked only at higher molecular weights and at higher polymer concentrations, and, on

TABLE 5

Results of the Step Injection Experiment Measured at a Flow-Rate of 0.334 ml/min

Specific Viscosity Step	μ'_1	μ_2	μ_3	N	A_{exp} $.10^{-3}$	A_{theor} $.10^{-3}$
Benzene into THF	152.2	134.6	360	172	0.102	0.135
+0.404	140.7	468.6	8001	42.2	2.87	2.24
+1.319	146.6	525.6	14567	40.9	4.62	2.39
+2.224	147.4	340.3	5487	63.8	1.71	0.98
-0.239	133.0	459.4	8077	38.5	3.43	2.70
-0.514	130.1	409.7	6442	41.3	2.92	2.35
-1.170	134.2	857.2	42575	21.0	17.6	9.07

the other, by the tendency of macromolecules to concentrate in the centre of the capillary. Thereby the viscosity in the centre of the capillary increases in consequence of which the velocity in the capillary centre decreases. This phenomenon can cause "by-pass" of the cloud of the polymer solution at higher concentration by that having a lower concentration in the proximity of the wall. In accord with this is also a steeper slope of the dependence of μ'_1 on η_{spec} at the higher flow-rate for the pulse injection experiment the explanation of which was presented above on the basis of Eqns. (19) and (20).

The tendency of macromolecules or particles to concentrate in the centre of the capillary can be explained by the lift forces (22) which were observed experimentally by several authors (9-11, 23), as mentioned already above.

The theoretical value of asymmetry is in a very good agreement with the experimental value for the elution of benzene. The ratio of other values A_{theor}/A_{exp} is on average ca. 0.5, i.e., tailing is greater than assumed by the theoretical model.

Much more marked are differences in $/u_1'$ at the higher flow-rate when the influence of the radial diffusion of polymer solute is almost neglectable, under the given conditions of the segregated flow. On the injection of the solution of PS standard into THF $/u_1'$ is by 5 % lower in comparison with $/u_1'$ on the injection of benzene into THF. On the injection of THF into the solution of PS standard the values of $/u_1'$ are by 13 % lower than the values of $/u_1'$ for benzene. These facts confirm that the influence of the radial diffusion is really slight and therefore the zone front moves, owing to a higher linear velocity in the capillary centre, at a much higher speed. Further it is obvious that in the case of the injection of THF into the solution of PS standard, occurs "break-through" of the zone of the PS solution by much less viscous and thus more mobile THF. The ratio A_{theor} / A_{exp} lies in the range 0.52 - 0.80 and is on average by 15 % higher than at the lower flow-rate. Examples of the elution curves from the step injection experiment are shown in Figs. 3 and 4.

Slight and non-systematic influence of η_{spec} on $/u_1'$ in the both instances of the low and the high flow-rates indicates that the shape of the velocity profile is a dominant factor and hence it is convection that governs transport processes at the both boundaries

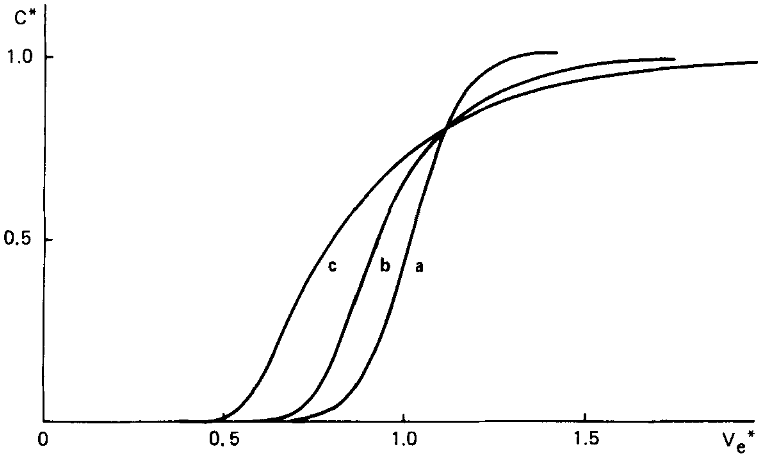

FIGURE 3
Normalized chromatograms of benzene and PS 4 standard injected as steps at various concentrations at a flow-rate of 0.334 ml/min.
a...benzene, b... $\eta_{spec} = +2.224$, c... $\eta_{spec} = -1.170$
C^*, Ve^* normalized concentration and elution volume

and in the polymer zone under the given conditions of the flow.

The above results are in a good agreement with the calculations by Hess and Tierney (5) who found out that a decrease in the maximal velocity in the capillary centre, caused by the flattening of the originally parabolic velocity profile during the flow of polymer solutions, is of the order of per cents (depending on the molecular weight and the concentration).

Further experimental and theoretical studies of the shape of the velocity profile on the solvent-

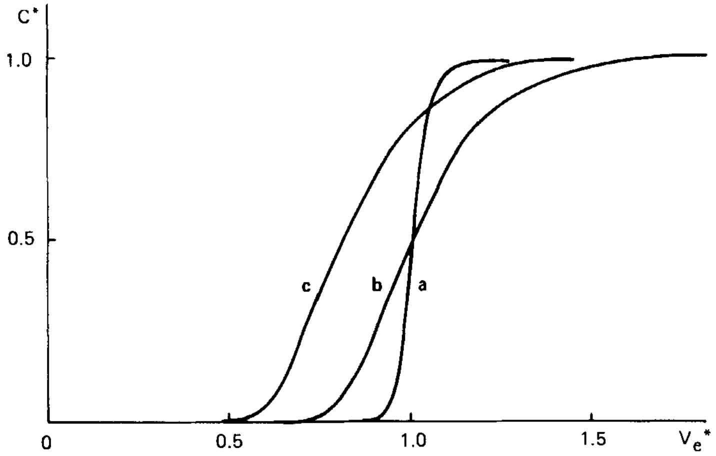

FIGURE 4
Normalized chromatograms of benzene and PS 4 standard injected as steps at various concentrations at a flow-rate of 0.038 ml/min.
a...benzene, b... η_{spec}= +0.872, c... η_{spec}= -0.514.
C^*, Ve^* normalized concentration and elution volume

-polymer solution or polymer solution-solvent boundary are in progress.

ACKNOWLEDGEMENT

Experimental assistance of Mrs. P. Neureutterová is gratefully acknowledged.

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