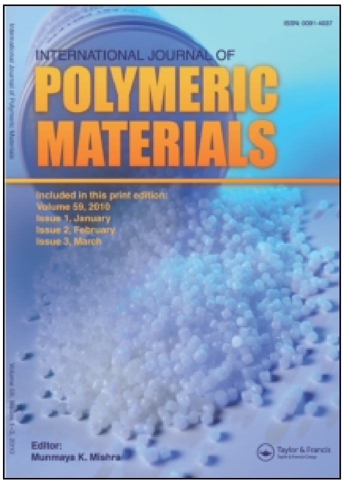

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Polymer-Solvent Interaction from Gas-Liquid Chromatography. Initial Experiments with Open Tubular Columns†

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Open tubular columns coated with polymer above its glass transition temperature have been used for measuring polymer-solvent interactions with gas-liquid chromatography. Consideration is given to the effect of polymer-film thickness on polymer-solvent interaction. Experimental retention volumes are reported for a number of solvents with poly (isobutylene) at 75°C and with poly(dimethylsiloxane) at 70°C and compared with those obtained using packed columns.

1 INTRODUCTION

Gas-liquid chromatography (GLC) shows much promise as a technique for rapid measurement of polymer-solvent interactions in highly concentrated polymer solutions. Several recent articles have discussed application of the method.[1-5] At the present time thermodynamic measurements with GLC are made exclusively in packed columns, where the polymer is coated onto a solid support. These columns are easy to prepare with an accurately known amount of polymer. Their primary disadvantage is that the maximum attainable film thickness is only about 1000 Å, which is the order of magnitude of the length of a polymer molecule. The important question therefore arises whether the interactions in such a thin polymer film are the same as those in a bulk polymer. It is likely that the degree of order in a thin film of polymer, adsorbed on a solid support, is different from that of a bulk polymer.

To determine the effect of polymer-film thickness on polymer-solvent

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† Presented at the Midland Macromolecular Meeting on "Order in Polymer Solutions", August 20–24, 1973.

interactions, thermodynamic measurements with GLC in open tubular columns may be helpful. These columns are prepared by coating the polymer onto the inside wall of a small bore tube; no granular packing material is used. The film thickness in these columns is about 1–10 × 10^4 Å and can be varied systematically.[6] However, it is difficult to determine the exact amount of stationary phase in the column. Therefore open tubular columns have rarely been used for thermodynamic measurements,[7,8] but so far agreement was found always with packed columns. However, polymers were not used for any of these measurements. Recently Newman[9] made a few preliminary experiments using open tubular columns coated with polymers. His results did not lead to a clear conclusion concerning possible effects of the polymer-film thickness on polymer-solvent interaction.

In this work we report some initial studies which suggest that activity coefficients measured in open tubular columns are in agreement with those measured in packed columns provided proper corrections are made for the effect of carrier-gas flow rate.

2 EXPERIMENTAL

2.1 Apparatus

The gas chromatograph used was a Varian Aerograph 1520 equipped with a Hamilton 86800 injector and a Carle model 1000 micro thermistor detector; a schematic diagram is shown in Figure 1. Column-oven temperature was controlled by a Hallikainen Instrument thermotrol to within ±0.1°. Flow of helium carrier gas was measured at the outlet by a soap bubble flowmeter and controlled by a Negretti and Zambra precision regulator valve. Pressure at the inlet and outlet was measured to within 0.1 mm with a mercurymanometer. Liquid solutes were injected through a silicone rubber septum using a 1 μl Hamilton syringe.

2.2 Preparation of columns

In the packed columns the stationary phases were coated onto Chromosorb P or onto Chromosorb W (both AW-DMCS) by dissolution in chloroform or toluene, mixing, and slow evaporation. When constant weight was attained, the coated support was packed into 1.5 m of 0.635 cm stainless-steel tubing. The average polymer-film thickness is calculated from the volume of the polymer and the surface area of the support.

Preparation of open tubular columns and their use is discussed in detail by Ettre.[10] In this work we used stainless-steel columns, i.d. 0.075 cm, 20 meters long, with a wall thickness of 0.038 cm. Before coating the columns were carefully cleaned with several solvent washes as described by Mon.[11] The dynamic method of coating was chosen, and Figure 2 shows a schematic diagram of the apparatus used for this procedure. In this method about

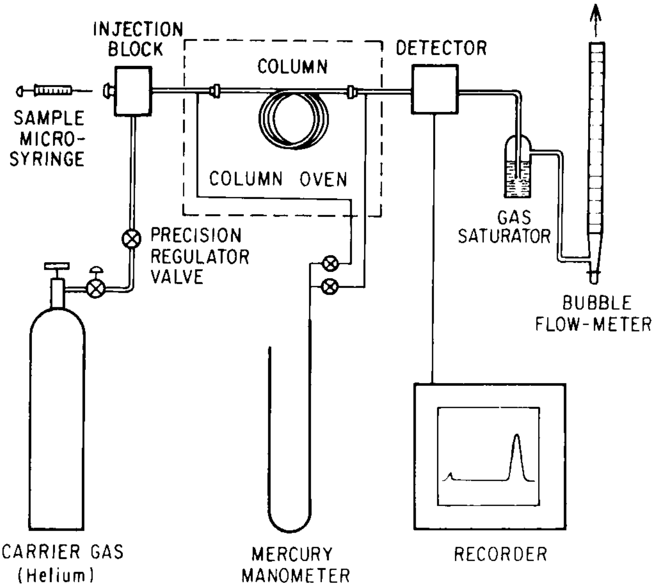

FIGURE 1 Gas chromatographic apparatus. Reprinted from Ref. (5) by courtesy of the American Chemical Society.

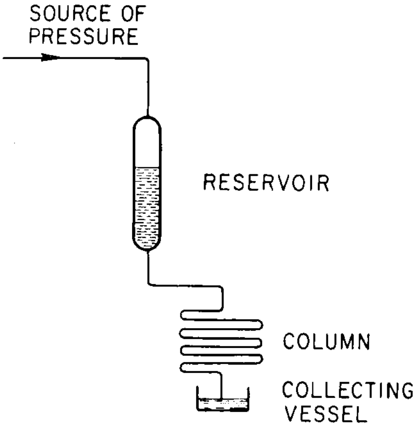

FIGURE 2 Schematic diagram of the dynamic method of coating open tubular columns with the liquid phase.

10 cm^3 of a dilute polymer solution (6–10 wt % of polymer in chloroform or toluene) are placed in the reservoir and pushed through the column with nitrogen at about 0.5 atm gauge. Continued nitrogen flow dries the polymer solution which adheres to the tube wall, leaving a coating of polymer. A 10 cm^3 portion of the coating solution is put through the column as many times as it takes to obtain a film thickness of the order of 10^4 Å. The amount of polymer in the column is determined by careful weighing of the column before and after coating. A suitable high-precision balance is required because the weight of the column itself is several orders of magnitude larger than that of the adhering polymer. By careful handling and drying of the column in an oven, weighings reproducible to ± 0.4 mg (*i.e.*, ± 0.5 %) were obtained.

The average film thickness for the columns is calculated from the volume of polymer and the inside surface area of the tube.

Table I shows details of column preparation. We have no guarantee that we have a completely uniform coating of the open tubular columns. However, the variation in polymer film thickness for these columns is probably no worse than that for packed columns.

2.3 Stationary phases and solutes

Poly(isobutylene) ($\overline{M}_\eta = 5.3 \times 10^4$) was obtained from Enjay Chemical Co., and poly(dimethylsiloxane) ($\overline{M}_\eta = 6 \times 10^5$) was obtained from Cellomer Corp., Webster, N.Y. The solutes used were reagent grade materials obtained from standard supply sources. Since solute purity is not of major importance in these measurements, they were used without further purification.

Solute sample size was kept as small as possible, to avoid overloading of the columns. For the packed columns the samples were always less than 0.1 μl and for the open tubular columns samples of the order of 0.01 μl were used because of the small column volume. Variation of the sample size did not affect the peak maximum retention time.

2.4 Data reduction

Patterson, Tewari, Schreiber and Guillet[3] have discussed how activity coefficients may be obtained from quantities measured by GLC. Their equation is

$$\ln \gamma_1^\infty = \ln \left(\frac{273.2R}{P_1^s V_g^0 M_2} \right) - \frac{P_1^s(B_{11} - V_1)}{RT} \tag{1}$$

where subscript 1 refers to the volatile component and supscript 2 refers to the polymer, γ_1^∞ is the infinite-dilution activity coefficient based on mole fraction, M_2 is the molecular weight, R is the gas constant, P_1^s is the saturation

TABLE I

Chromatographic columns

Column characteristics	Packed		Open tubular			
	1	2	3	4	5	6
Polymer	PIB	PDMS	PIB	PIB	PDMS	PDMS
Support	Chrom-P	Chrom-W	none	none	none	none
Weight of polymer, g	2.0995	0.9047	0.2307	0.3813	0.1616	0.1035
Weight of support, g	7.7860	10.0002	—	—	—	—
Length of column, m	1.5	1.5	20	20	20	20
Column i.d., cm	0.491	0.491	0.075	0.075	0.075	0.075
Film thickness, Å	4.6×10^2	4.6×10^2	5.1×10^4	8.6×10^4	3.5×10^4	2.4×10^4
Coating solvent	chloroform	toluene	chloroform	chloroform	toluene	toluene

vapor pressure at temperature T, V_1 is the liquid molar volume at T, V_g^0 is the specific retention volume corrected to 0°C, and B_{11} is the second virial coefficient if pure 1 at T.

Patterson *et al.*[3] point out that the activity coefficient given by Eq. (1) is not convenient for polymer-solvent systems since the polymer molecular weight must be accurately known and the logarithm of the activity coefficient tends to $-\infty$ as $M_2 \rightarrow \infty$. They propose the following equation based on weight fraction w:

$$\ln \Omega_1^{\infty} = \ln \left(\frac{a_1}{w_1}\right)^{\infty} = \ln \left(\frac{273.2R}{P_1^s\, V_g^0\, M_1}\right) - \frac{P_1^s}{RT}(B_{11} - V_1) \qquad (2)$$

where Ω^{∞} is the weight fraction activity coefficient at infinite dilution. Either of these equations may be used to calculate the Flory-Huggins interaction parameter.

The quantity V_g^0 in these equations is given by

$$V_g^0 = Q(t_r - t_g)\,\frac{273.2}{T}\,\frac{f_p}{W_2} \qquad (3)$$

where Q is the volumetric carrier gas flow rate at column outlet temperature and pressure, cm^3/min; $(t_r - t_g)$ is the retention time, *i.e.*, the time difference between air and solvent peaks, in min; T is the column temperature, °K; W_2 is the weight of polymer in the column, g; and f_p is the pressure correction term[12]

$$f_p = \frac{3}{2}\left(\frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}\right) \qquad (4)$$

where P_i is the inlet pressure and P_0 is the outlet pressure.

To determine the effect of the polymer-film thickness it is not necessary to calculate the activity coefficients, but it is sufficient to compare the specific retention volumes.

3 RESULTS AND DISCUSSION

At a given temperature the GLC-measurements were performed at various flow rates for a variety of solvents. Equation (3) was used to calculate the peak maximum retention volumes. Figure 3 shows the flow rate dependence of the specific retention volume for PIB at 75°C obtained with the open tubular columns together with the packed column results reported by Newman.[9] For all three solvents V_g^0 increases with decreasing flow rate of the carrier gas. To obtain the "real" retention volume, one has to extrapolate to zero flow rate in order to assure that equilibrium was obtained. For this purpose

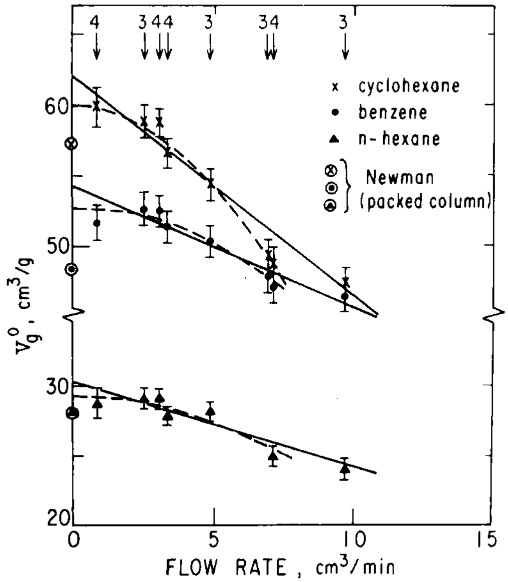

FIGURE 3 Flow rate dependence of the specific retention volume V_g^0 for poly(isobutylene) — hydrocarbon systems at 75°C (numbers 3 and 4 refer to the column code in Table I.

Newman simply used a linear extrapolation. However, at very low flow rates V_g^0 should not be a function of the flow rate, *i.e.*, the intercept with the ordinate in Figure 3 should be reached with zero slope. For extrapolation to zero flow rate we therefore propose†

$$V_g^0 = a \exp(-b\,Q^2) \tag{5}$$

where a and b are constants characteristic for each polymer-solvent pair. If the flow rate dependence of V_g^0 is given by Eq. (5), a plot of ln V_g^0 versus Q^2 must be a straight line; this was obtained for the three solvents used in this work as shown in Figure 4. At least at flow rates below 7 cm³/min Eq. (5) is valid; this is precisely the range which is most important for extrapolation to zero flow rate. The flow rate dependence according to Eq. (5) is also shown in Figure 3 (dashed lines). Equation (5) gives better agreement with the experimental values than the simple linear function. The difference of the "real" V_g^0 obtained by linear and non-linear extrapolation is for all three solvents only slightly larger than the experimental error (±2.5% at flow rates below 1 cm³/min). Nevertheless, non-linear extrapolation should be

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†A more detailed discussion of Eq. (5) is given in the Appendix.

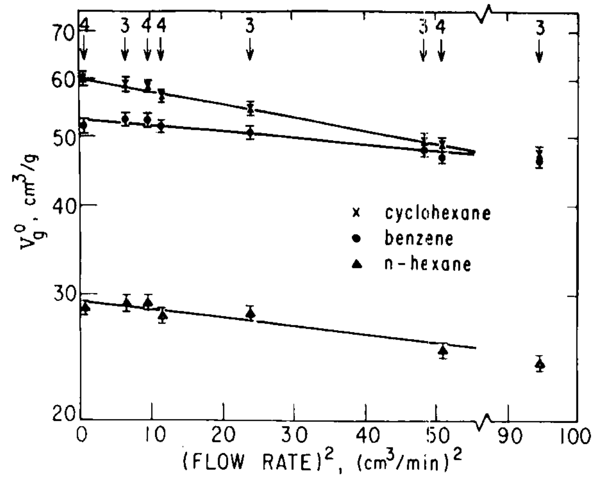

FIGURE 4 Flow rate dependence of the specific retention volume V_g^0 for poly(isobutylene)—hydrocarbon systems at 75°C (numbers 3 and 4 refer to the column code in Table I).

preferred on principle. There is no effect of the polymer-film thickness on the determined retention volumes observed, although the thicknesses of the PIB film of the two open tubular columns differ by about a factor two. However, the retention volumes Newman obtained with packed columns are considerably lower than our values. The thickness of the PIB film in Newman's packed column was 4.6×10^2 Å, *i.e.*, by a factor of 100 less than in our open tubular column. Hence one is tempted to attribute the discrepancy of the results to the difference in the film thickness. But this conclusion is tentative as we do not know how good Newman's packed column results are. At 50°C, for example, Newman has observed flow rate dependence, not, however, at 75°C. Our open tubular column results indicate a strong flow rate dependence also at 75°C. It is difficult to understand why a similar effect is not present in packed columns. If there was flow rate dependence which Newman failed to recognize, his results must be too low (as they seem to be) and the discrepancy could be explained. This presumption is confirmed by the results for the PDMS systems, which are shown in Table II. The measurements in the open tubular columns were performed at various flow rates. There appears to be no dependence of V_g^0 on the flow rate. Table II also reports specific retention volumes obtained with packed columns. The results from both types of columns agree fairly well, although the open tubular column results are mostly somewhat lower. The average film thickness in the packed column was about 4.6×10^2 Å, whereas both open tubular columns had a film thicker than

TABLE II

Specific retention volumes V_g^0 (cm^3/g) for poly(dimethylsiloxane)—hydrocarbon systems at 70°C for various flow rates

	Column code							
	Packed	Open tubular						
Solvent	2	6	5	6	5	6	5	5
Flow rate, cm^3/min	—	2.22	2.88	3.07	4.15	4.55	5.20	5.94
n-pentane	19.46	19.53	19.30	—	19.42	19.68	—	19.58
n-hexane	44.10	43.16	41.80	—	42.84	42.80	—	42.72
n-heptane	96.59	—	—	—	96.02	97.80	—	97.22
n-octane	209.4	—	—	209.4	210.1	206.1	205.8	211.6
Cyclohexane	73.55	72.06	71.63	—	—	71.95	71.46	73.40
Cycloctane	502.3	—	—	493.3	494.1	496.8	494.9	501.7
Benzene	68.45	66.42	66.00	66.59	—	67.51	—	68.16
Tert-butyl-benzene	823.3	—	—	—	—	804.5	—	815.6
2-methyl-pentane	34.90	33.76	33.01	—	—	—	—	33.89

2 × 10^4 Å. Again one may conclude that the lower values obtained with the open tubular columns are due to the difference in the film thickness.

For both polymers used in this work we therefore believe that there is an effect of the polymer-film thickness on polymer-solvent interactions, although this conclusion might be premature. To confirm this conclusion more experimental results at various temperatures will be necessary.

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Added in proof: (a) Recomputation of Newman's experimental data[9] showed that he used a wrong value for the weight of polymer in the column in his calculations for PIB. When the correct weight W_2 is used Eq. (3) yields about 10% higher retention volumes. The conclusion of this paper is not altered by this means. (b) A more detailed study on open tubular columns is published by the authors in *Macromolecules* **7**, 565 (1974).

Appendix

For the calculation of activity coefficients from the experimentally determined retention volumes one needs ln $V_g{}^0$. Also, theory suggests that ln $V_g{}^0$ should be a nearly linear function of $1/T$. Therefore, ln $V_g{}^0$ rather than $V_g{}^0$ appears to be the preferred variable. We suggest that

$$V_g{}^0 = e^{-g(Q)} \tag{A1}$$

where $g(Q)$ is a function of the flow rate. For extrapolation to zero flow rate the low flow rates are of special interest; $g(Q)$ is therefore written as a Taylor series at $Q = 0$

$$g(Q) = g(0) + \frac{Q}{1!}g'(0) + \frac{Q^2}{2!}g''(0) + \ldots \tag{A2}$$

The slope of the $V_g{}^0$ *vs.* Q dependence at zero flow rate should be zero, $(dV_g{}^0/dQ)_{Q=0} = 0$. From this condition it follows that $g'(0) = 0$. Combining Eq. (A1) with Eq. (A2) and neglecting terms higher than Q^2 (we are extrapolating to $Q = 0$), one obtains:

$$V_g{}^0 = \exp[-g(0) - \tfrac{1}{2}g''(0)Q^2] \tag{A3}$$

This equation is the same as Eq. (5) in the text where $a = e^{-g(0)}$ and $b = g''(0)/2$. Neglecting higher terms than Q^2 may explain why Eq. (5) fails at higher flow rates.