References and Notes

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(9) Recent considerations (M. Randić, to be published) of heats of atomization indicated an impressive agreement with experimental values for large number of mono olefins, of each bond kind, namely C—C, C—C, and C—H, are described by *two* parameters (*i.e.*, a linear relationship between bond overlap and bond energy, instead of frequently assumed proportionality). Calculated heats of atomization are with ±3 kcal/mol from the experimental values with a further improvement in sight.
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Polymer–Solvent Interactions from Gas–Liquid Chromatography with Capillary Columns

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ABSTRACT: To determine the effect of polymer-film thickness on thermodynamic properties, capillary columns and packed columns were used to measure polymer–solvent interactions. Experimental retention volumes at 50–175° are reported for several solvents with poly(isobutylene), poly(vinyl acetate), and poly(dimethylsiloxane). The capillary-column results are often strongly sensitive to gas flow rate, probably because of the large time required to attain equilibrium between solvent and a polymer film whose thickness is in the range 10^4–10^5 Å; in packed columns the film thickness is about two orders of magnitude smaller. When capillary-column data are extrapolated to zero flow rate, the retention volumes differ from those obtained with packed columns, sometimes by as much as 20%; this difference, however, decreases to 5% or less at higher temperatures. For poly(isobutylene) with benzene and with cyclohexane, Flory χ parameters obtained with capillary columns appear to be in better agreement with those obtained from static data than are those measured in packed columns. The results obtained in this work suggest that polymer–solvent interactions for a bulk polymer may be different from those for a thin polymer film adsorbed on a granular packing.

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.[2-5] In all previous work, thermodynamic measurements for polymers with glc have been 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 and, with a little experience, much data can be obtained rapidly. Their primary disadvantage is that the maximum attainable film thickness is only about 10^2 or 10^3 Å, which is the order of magnitude of the length of a polymer molecule. The important question therefore arises whether the polymer–solvent interactions in such a thin polymer film, adsorbed on a granular solid, are the same as those in a bulk polymer. It appears likely that the morphology, or the degree of order, in a thin film of polymer, adsorbed on a solid support, is different from those of a bulk polymer.

To determine the effect of polymer–film thickness on polymer–solvent interactions, we report here thermodynamic measurements with glc in capillary (open tubular) columns. These columns are prepared by coating the polymer onto the inside wall of a small-bore tube; no granular

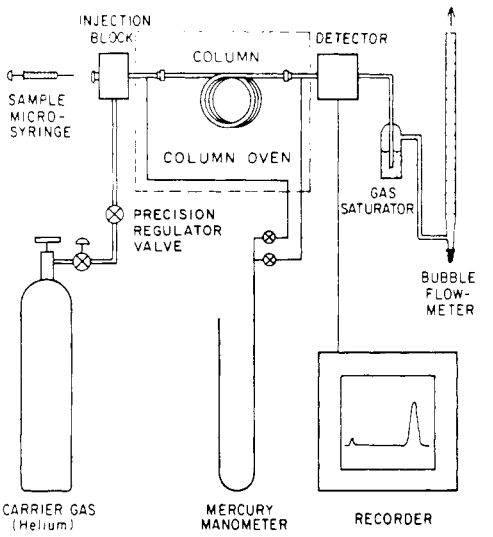

Figure 1. Gas chromatographic apparatus.

packing material is used. The film thickness in these columns is in the range 10^4–10^5 Å and can be varied systematically.[6] However, it is difficult to determine the exact amount of stationary phase in the column. Therefore, capillary columns have rarely been used for thermodynamic measurements[7,8] but, for the few cases where data were reported, fair agreement was found with results obtained with packed columns. However, in all previous measurements with capillary columns, ordinary liquids, not polymers, were used as the stationary phase. Recently Newman[9] made a few preliminary experiments using capillary columns coated with polymers but his results did not lead to a clear conclusion concerning possible effects of polymer film thickness. In this work we report experimental results which suggest that activity coefficients measured in capillary columns may differ from those measured in packed columns.

Experimental Section

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 Co. 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 mercury manometer. Liquid solvents were injected through a silicone rubber septum using a 1-μl Hamilton syringe.

In the packed columns the stationary phases were coated onto Chromosorb P or onto Chromosorb W (both AW-DCMS) 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 capillary 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 m 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 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 which adheres to the tube's inner wall. 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

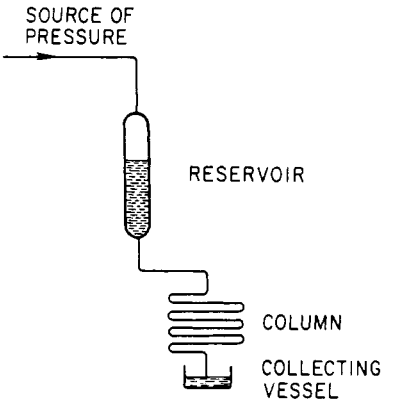

Figure 2. Schematic diagram of the dynamic method of coating capillary columns with the liquid phase.

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 were obtained; the polymer weight is therefore accurate to within ±0.5%.

The average film thickness for the column 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 capillary columns. However, the variation in polymer film thickness for these columns is probably no worse than that for packed columns. The average film thickness in the capillary columns is in all cases about two orders of magnitude larger than that in the packed columns.

Stationary Phases and Solvents. Poly(isobutylene) (PIB) ($\bar{M}_v$ = 53,000) was obtained from Enjay Chemical Co. and poly(vinyl acetate) (PVA) ($\bar{M}_w$ = 331,400 by light scattering) and poly(dimethylsiloxane) (PDMS) ($\bar{M}_v$ = 600,000) were obtained from Cellomer Corp., Webster, N. Y. The solvents used were reagent-grade materials obtained from standard supply sources. Since solvent purity is not of major importance in these measurements, they were used without further purification.

Solvent 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 (~10^{-9} g-mol) were used because of the small column volume. Alteration of the sample size did not affect the peak maximum retention time.

Data Reduction. Patterson *et al.*[3] point out that the activity coefficient for a solvent in a polymer solution is most conveniently defined on a weight fraction basis. At infinite dilution the activity coefficient Ω_1^∞ is given by

$$\ln \Omega_1^\infty = \ln \left(\frac{a_1}{w_1}\right)^\infty = \ln \left(\frac{273.15R}{P_1^s V_g^0 M_1}\right) - \frac{P_1^s}{RT}(B_{11} - V_1) \quad (1)$$

where subscript 1 refers to the volatile component and subscript 2 to the polymer; a_1 is the activity; w_1 is the weight fraction; M_1 is the molecular weight; R is the gas constant; P_1^s is the saturation 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°; and B_{11} is the second virial coefficient of pure 1 at T.

The quantity V_g^0 is given by

$$V_g^0 = Q(t_r - t_g)(273.15/T)(f_P/W_2) \quad (2)$$

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, 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 given by Purnell[12]

$$f_P = \frac{3}{2}\left(\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right) \quad (3)$$

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

Table I
Chromatographic Columns

Column Code	Packed			Capillary				
	1	2	3	4	5	6	7	8
Polymer	PIB	PDMS	PVA	PIB	PIB	PDMS	PDMS	PVA
Support	Chrom-P	Chrom-W	Chrom-P	None	None	None	None	None
Weight of polymer, g	2.0995	0.9047	3.0288	0.2307	0.3813	0.1616	0.1035	0.2068
Weight of support, g	10.0002	7.7860	12.0365	-	-	-	-	-
Length of column, m	1.5	1.5	1.5	20	20	20	20	20
Column i.d., cm	0.491	0.491	0.491	0.075	0.075	0.075	0.075	0.075
Film thickness, Å	4.6×10^2	4.6×10^2	5.2×10^2	5.1×10^4	8.6×10^4	3.5×10^4	2.4×10^4	1.8×10^4
Coating solvent	Chloroform	Toluene	Chloroform	Chloroform	Chloroform	Toluene	Toluene	Chloroform

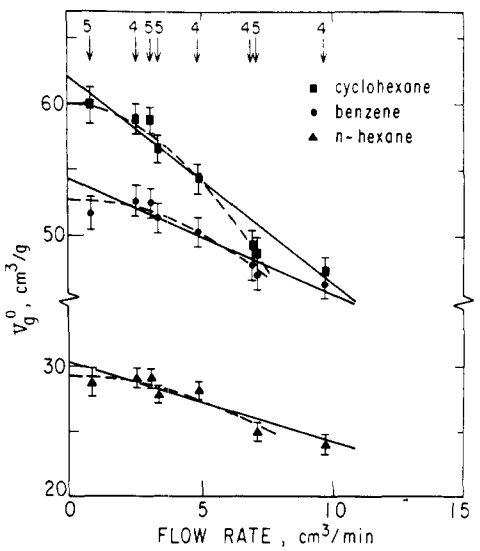

Figure 3. Effect of the flow rate on the specific retention volume V_g^0 for poly(isobutylene) systems at 75°; linear (——) and nonlinear (– – –) flow rate dependence (numbers 4 and 5 refer to the column code in Table I).

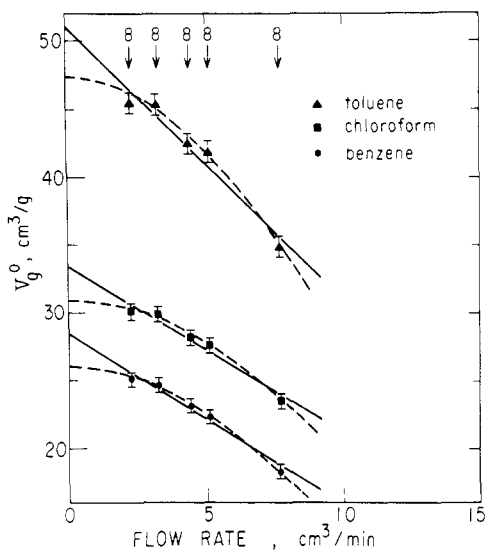

Figure 4. Effect of the flow rate on the specific retention volume V_g^0 for poly(vinyl acetate) systems at 100°; linear (——) and nonlinear (– – –) flow rate dependence (number 8 refers to the column code in Table I).

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

Results and Discussion

For both types of columns, glc measurements at a given temperature were performed at several flow rates for a variety of solvents. Equation 2 was used to calculate the peak maximum retention volumes. Each final value of V_g^0 is the average of at least three glc measurements. The peak maximum, rather than the intercept of the tangents to the flanks of the peak, was chosen to determine the retention time, because the former was reproducible, whereas the latter depended somewhat on the attenuation of the recorder used to plot the signal from the thermal conductivity detector.

With capillary columns, tailing peaks were obtained for all three polymers; tailing was much stronger for PIB and for PVA than for PDMS. According to Young[13] there are three main causes for peak asymmetry: (1) isotherm curvature, (2) surface adsorption, and (3) nonequilibrium. In capillary columns asymmetry is also caused by the laminar flow of the carrier gas in the tubing.

For a nonlinear sorption isotherm, at very low concentration of solvent (*i.e.*, small sample size), a condition very close to linearity can be achieved and then the obtained peaks should be almost symmetrical.[14] In our experiments, however, the asymmetry remained unchanged even with the smallest sample size we could handle. Isotherm curvature is therefore not a significant cause for our tailing peaks.

To correct for the effect of surface sorption, Conder[15] suggests that the retention volume consists of two contributions, one due to bulk sorption, and the other to surface sorption. If surface sorption is of importance, then retention volume data, taken on a series of columns having different loadings, would be different. In such a case extrapolation to infinite loading would be necessary in order to obtain the retention volume only due to bulk sorption. In our measurements with both types of columns we did not observe any dependence of the retention volumes on the loading and we therefore conclude that the effect due to surface adsorption is negligible in our work.

The effect of the laminar flow of the carrier gas in the tubing is significant especially at very low flow rates, but even then it causes only slightly skewed peaks. This effect was seen in our air peaks which skewed only slightly and had little tailing.

Tailing peaks may result from slow diffusion of the solvent vapor in the stationary phase; depending on the polymer film thickness and the flow rate, therefore, equilibrium may not be achieved.[16] In such a case, the peak maxima, where detectable, occur at lower retention times so that the apparent peak retention volumes are lower than those corresponding to equilibrium. The effect of slow equilibration can be eliminated by measuring the variation in peak re-

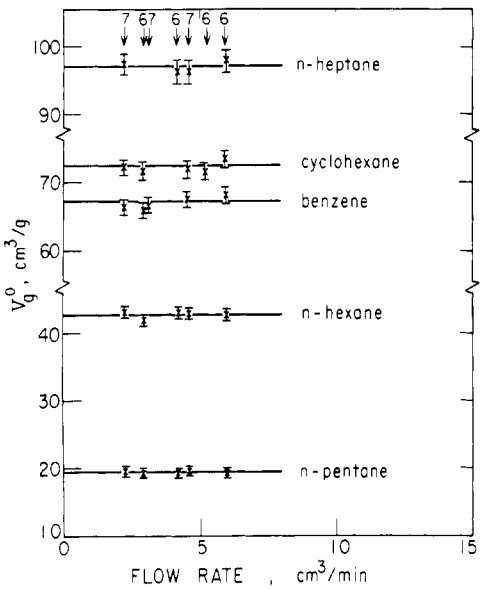

Figure 5. Effect of the flow rate on the specific retention volume V_g^0 for poly(dimethylsiloxane) systems at 70° (numbers 6 and 7 refer to the column code in Table I).

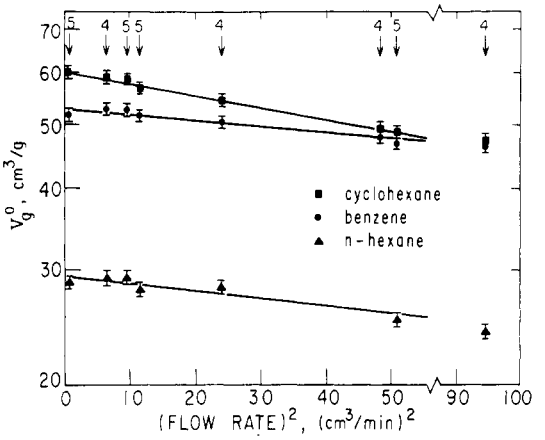

Figure 6. Flow rate dependence of the specific retention volume V_g^0 for poly(isobutylene) systems at 75° (numbers 4 and 5 refer to the column code in Table I).

tention volume with flow rate and extrapolating to zero flow rate. Therefore, glc measurements were performed at various flow rates. The flow rate dependence of the specific retention volume is shown in Figure 3 for PIB systems at 75°, in Figure 4 for PVA systems at 100°, and in Figure 5 for PDMS systems at 70°. No flow rate dependence is observed for any of the PDMS systems, whereas for all PIB systems and for all PVA systems V_g^0 increases with decreasing flow rate of the carrier gas. This behavior was expected, as the observed tailing of the peaks is strong for all PIB and PVA systems, whereas it is small for the PDMS systems and for the latter seems to be only due to laminar flow.

To obtain retention volumes corresponding to equilibrium, Newman[9] used a linear extrapolation to zero flow rate. 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 Figures 3–5 should be reached with zero slope. For extrapolation to zero flow rate we therefore propose

$$V_g^0 = a \exp(-bQ^2) \quad (4)$$

where a and b are temperature-dependent constants, characteristic for each polymer–solvent pair. (A more detailed discussion of eq 4 is given in the Appendix.) If the flow rate dependence of V_g^0 is given by eq 4 a plot of ln V_g^0 *vs.* Q^2 must be a straight line. Straight lines were, in fact, obtained for all the systems used in this work as shown in Figure 6 for PIB and in Figure 7 for PVA. The data indicate that at flow rates below ~7 cm³/min, eq 4 appears to be valid; this is precisely the range which is the most important for extrapolation to zero flow rate. The flow rate dependence according to eq 4 is also shown by the dashed lines in Figures 3 and 4. Especially at low flow rates eq 4 gives a better representation of the experimental values than does a simple linear function. For PIB systems the difference of the zero flow rate V_g^0 obtained by linear and nonlinear extrapolation is only slightly larger than the experimental error (±2.5% at flow rates below 1 cm³/min), whereas for the PVA systems the zero flow rate values of V_g^0 differ by about 10%. Consequently the way of extrapolating to zero flow rate significantly affects the retention volumes corresponding to equilibrium. Results similar to those shown in Figures 6 and 7 were obtained at all temperatures investigated. In every case eq 4 gave a good representation of the experimental results. As temperature rises, the constant b declines.

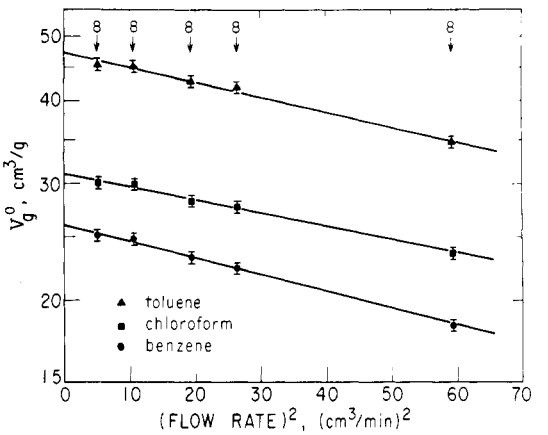

Figure 7. Flow rate dependence of the specific retention volume V_g^0 for poly(vinyl acetate) systems at 100° (number 8 refers to the column code in Table I).

The measurements with capillary columns for each of the PIB and the PDMS systems were performed in two columns differing in polymer film thickness. For both polymers there is no effect of polymer film thickness on the retention volumes, although the film thicknesses differ by about a factor of about two in both cases.

Specific retention volumes obtained with the capillary columns (by nonlinear extrapolation to zero flow rate) are given in Table II at all temperatures and for all polymer–solvent systems used in this work. The error analysis yields an accuracy of ±2.5% for the reported results.

Table II shows also experimental specific retention volumes measured with packed columns. These results agree well with those reported by Hammers and de Ligny.[2b] With packed columns the peaks shown on the recorder were consistently symmetrical and no flow rate dependence of the peak maximum retention volume was observed for any of the polymers. The reported results are somewhat more accurate (±1.5%) than those obtained with the capillary columns.

Comparison of Results Obtained with Packed and Capillary Columns

Retention volumes obtained with capillary columns are always lower than those obtained with packed columns, ex-

Table II
Specific Retention Volumes V_g^0 (cm^3/g) Obtained with Capillary and with Packed Columns[a]

	Capillary	Packed	Capillary	Packed	Capillary	Packed	Capillary	Packed
				PIB				
Temp (°C):	50		75		100		125	
n-Hexane	62.7	–	29.4	33.4	15.3	16.8	–	9.3
Cyclohexane	126	–	60.5	67.0	31.0	33.1	–	18.1
Benzene	112	–	52.7	56.1	27.5	29.7	–	16.0
				PVA				
Temp (°C):	100		125		150		175	
Chloroform	30.9	36.9	18.1	–	–	11.0	7.16	6.80
Benzene	26.0	32.1	15.8	–	–	10.1	6.59	6.35
Toluene	47.3	55.8	25.1	–	–	15.3	9.41	9.40

	PDMS			
Temp (°C):	55		70	
	Capillary	Packed	Capillary	Packed
n-Pentane	29.4	29.7	19.5	19.5
n-Hexane	70.0	72.8	42.6	44.4
n-Heptane	164.0	169.5	97.0	96.6
Cyclohexane	118.5	122.3	72.3	73.5
Benzene	105.0	111.6	67.2	68.5

[a] Results for capillary columns based on nonlinear extrapolation to zero flow rate.

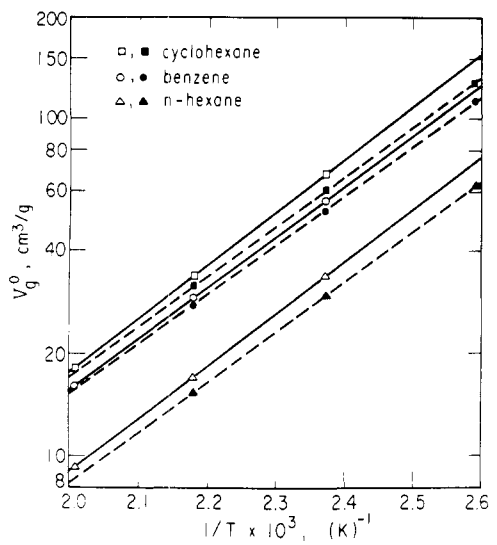

Figure 8. Temperature dependence of the specific retention volume V_g^0 for poly(isobutylene) systems; ——, packed columns; – – – –, capillary columns.

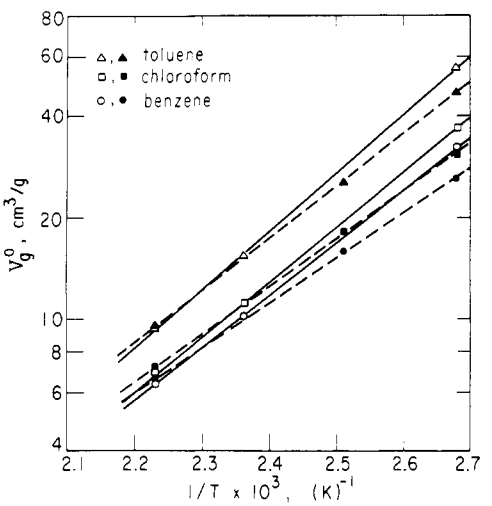

Figure 9. Temperature dependence of the specific retention volume V_g^0 for poly(vinyl acetate) systems; ——, packed columns; ———, capillary columns.

cept those for the PVA systems at 175°. With rising temperature, there is a decrease in the difference between results obtained with the two types of columns as shown in Figures 8 and 9, where ln V_g^0 is plotted *vs.* $1/T$ for the PIB systems and the PVA systems. Not only the results from capillary columns but also those from packed columns show that ln V_g^0 is a linear function of $1/T$, as suggested by theory. However, in all cases the slope of the lines for the packed columns is somewhat larger than that for the capillary columns.

Conclusion

Our experimental results show that there is a small but significant difference between retention volumes measured in a packed column and those measured in a capillary column. While the presently available evidence is not sufficient for a definite conclusion it appears that this difference in retention volumes is directly related to the large difference in polymer film thickness which distinguishes the two types of columns. In our capillary columns the film thickness is in the range $2–8 \times 10^4$ Å, while that in the packed column is about 5×10^2 Å.

It is reasonable to suspect that the thermodynamic properties of a thin polymer film, adsorbed on a solid (packing) surface, are different from those of a bulk polymer, especially when the film thickness is of the same order of magnitude as the polymer molecule's end-to-end distance.

As reported by several authors, notably Guillet,[17] there are small but systematic differences in Flory χ parameters from glc with packed columns and those from static measurements. In every case the χ parameter obtained from static measurements is either equal to or larger than that obtained from glc measurements. The Flory parameter at the polymer-rich end of a solution is given by

$$\chi = \ln \Omega_1^{\infty} - [\ln (v_1^*/v_2^*) + 1] \qquad (5)$$

where, for glc measurements, ln Ω_1^{∞} is related to retention volume V_g^0 as shown in eq 1. The specific hard-core volumes v^* are obtained from pure-component volumetric data.[18]

The Flory χ parameter from glc (packed columns) is generally lower than that extrapolated from static data. If film thickness is responsible, then that difference should markedly decrease when comparison is made between χ ob-

Table III
Flory χ Parameters for Poly(isobutylene) Systems from GLC and from Static Measurements[a]

Solvent	Temp (°C)	Glc: Packed Column	Glc: Capillary Column	Static[b]
Benzene	40	0.95	1.05	1.03[c]
	65	0.87	0.95	0.94[d]
Cyclohexane	40	0.56	0.64	0.64[d]
	65	0.50	0.62	0.64[d]

[a] These χ parameters are based on segment fraction, not volume fraction. [b] Extrapolated to infinite dilution from data at finite solvent concentration. Estimated uncertainty in χ due to extrapolation is ± 0.05. [c] B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64,** 2053 (1968). [d] C. E. H. Bawn and R. D. Patel, *Trans. Faraday Soc.*, **52,** 1664 (1956).

tained from static data and χ obtained from glc (capillary column). This decrease is, in fact, observed for two binary systems where the required data are available, as shown in Table III. Since static data are never obtained very close to compositions corresponding to infinite dilution for the solvent, there is always some question about uncertainties in extrapolation with respect to composition. However, for the two PIB systems shown in Table III it appears that results obtained with capillary columns are in better agreement with static results than are those obtained with packed columns.

For PDMS systems there is little difference between χ as obtained from any one of three experimental methods: static, glc (packed) and glc (capillary). Since the flexibility of PDMS is much larger than that of PIB,[19] it may well be that χ for PDMS systems is insensitive to film thickness while χ for PIB systems is not.

The results of this work suggest that while the chromatographic methods offer many operational advantages for characterizing polymer–solvent interactions, care must be taken in interpreting retention-volume data. Our studies support the reasonable assumption that polymer–solvent interactions for a thin polymer film are not necessarily the same as those for a bulk polymer.

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Appendix

Analytical Expression for Effect of Flow Rate on Retention Volumes. 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, at constant temperature

$$V_g^0 = \exp[-g(Q)] \tag{A1}$$

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 about $Q = 0$.

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

The intercept of V_g^0 *vs.* Q with the ordinate should have zero slope: $(dV_g^0/dQ)_{Q=0} = 0$. From this condition it follows that $g'(0) = 0$. Combining eq A1 with eq A2 and neglecting terms higher than Q^2, one obtains

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

Equation A3 is identical with eq 4 in the text where $a = \exp[-g(0)]$ and $b = g''(0)/2$. Neglecting terms higher than Q^2 may explain why eq 4 fails at higher flow rates.

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