Sorption of Solutes by Poly(ethylene Oxide).
I. Infinite-Dilution Studies

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Synopsis

Gas–liquid chromatography was used to study the equilibrium sorption by poly(ethylene oxide) of small amounts of 14 organic solutes and water between 70°C and 150°C at essentially atmospheric pressure. The effect of polymer degradation on the results is discussed and taken into account. Comparison between these results and those of other workers indicates fair agreement.

INTRODUCTION

The thermodynamics of concentrated polymer solutions has received increasing attention by researchers. During the last 30 years or more, many workers have measured solute activities over polymer solutions, usually using static equilibrium techniques that tend to be slow to reach equilibrium. In 1963, gas–liquid chromatography (GLC) was used for the first time to measure the activity coefficient of a vapor over a low molecular weight stationary phase.[1] GLC was not applied to a polymer stationary phase until 1969, when Smidsrød and Guillet[2] determined the activity coefficients of acetic acid, hexadecane, and butyl alcohol at infinite dilution (nearly zero solute concentration) in a polyamide of 50,100 molecular weight. Since 1969, infinite dilution results obtained using GLC have been reported by several investigators: Guillet and Stein,[3] Patterson et al.,[4] Hammers and Deligny,[5] Newman and Prausnitz,[6,7,8] Brockmeier et al.,[9,10,11] Cheng and Bonner,[12] and others. Both polar and nonpolar solutes have been studied at temperatures between 25°C and 200°C.

In this work, we have used GLC to study the equilibrium sorption by poly(ethylene oxide) (PEO) of small amounts of 14 organic solutes and water between 70°C and 150°C at essentially atmospheric pressure. Accurate knowledge of thermodynamic properties of concentrated solute/PEO solutions is valuable to the process designer for many industrial situations. For example, in the formulation of water-soluble packaging films, PEO is applied to a surface as a thin layer of concentrated solution, and then the solute evaporates from the polymeric film. The drying process designer requires knowledge of thermodynamic properties of concentrated solute/PEO solutions at different temperatures.

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Both solute specific retention volumes and infinite-dilution volatilities for solute/PEO solutions are presented and discussed here. Using direct measurement of solution vapor pressure, a "static" method, Booth and Devoy[13] have reported activity coefficients of benzene in PEO at 70°C. Comparison of their static results with our infinite-dilution GLC results shows fair agreement between the data obtained using the two methods.

EXPERIMENTAL

Apparatus and Procedure

Our gas–liquid chromatographic apparatus is shown schematically in Figure 1. For infinite-dilution operation, valve (3) is closed and valve (2) is opened. The GLC apparatus shown in Figure 1 is similar to that used by Newman and Prausnitz[6,7,8] when the constant-temperature oil bath, the liquid nitrogen condenser, and the heating along the tubing are not operated. These modifications are used for finite-concentration studies.

The gas–liquid chromatograph used is an F & M 500 equipped with a thermal conductivity detector. The column oven was rebuilt to provide oven-temperature control to ±0.1°C using a Hallikainen Thermotrol controller and to enable measurement of pressure drop through the column. Inlet and outlet column pressures are read to ±0.1 mm Hg with a mercury manometer. Carrier gas flow rate is measured to ±0.2 ml/min (at S.T.P.).

Helium carrier gas flows through a Negretti and Zambra flow regulator. Flow rates from the cylinder are controlled by valve (1) and are measured with a soap-bubble flowmeter. A small portion of carrier gas controlled by valve (4) goes through a reference line. A very small quantity of the solute (between 0.01 and 1 μl) and air are rapidly injected into the flowing helium through a silicone rubber septum with a 1.0-μl or 10-μl Hamilton gas-tight sy-
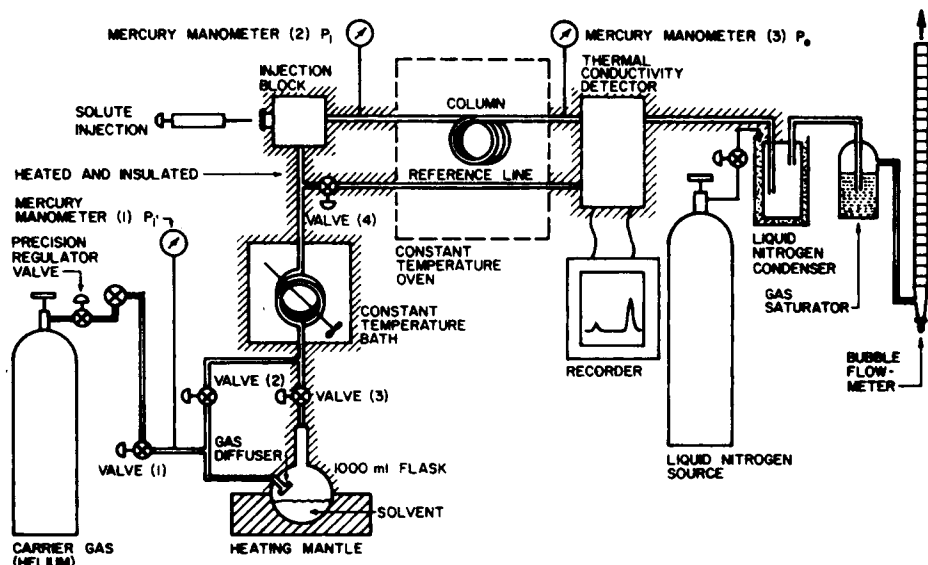

Fig. 1. Schematic diagram of modified gas–liquid chromatographic apparatus.

ringe. As the solute is vaporized in the injector block and carried into the chromatographic column, it is absorbed in the polymer to some extent. The solute then migrates down the column with the carrier gas. The amount of solute in carrier gas is continuously monitored by the thermal conductivity detector. Relative solute retention time is obtained by subtracting the residence time of the air from the residence time of the solute. Air is essentially inert with respect to the polymer. The residence time of the solute is defined as the time required to sweep the solute in the carrier gas from the column and is determined by the thermodynamic equilibrium between the solute and the polymer and by the space available for flow in the column. The time difference between the chromatogram peaks of solute and air, multiplied by the carrier gas flow rate, is the adjusted retention volume. The adjusted retention volume corrected for pressure drop within the column is related to the vapor–liquid equilibria of the solute between carrier gas and polymer, as discussed below. The column inlet and outlet pressures are read to correct column pressure for pressure drop.

Stationary Phase and Solutes

The PEO is Polyox WSR-301 supplied by the Union Carbide Corporation. Stone and Stratta[14] have reported that WSR-301 has a melting range of 65° ± 2°C, specific gravity of 1.21 g/cm^3 at 25°C, and approximate molecular weight of 4×10^6 g/g-mole.

The solutes used are reagent-grade materials supplied by various chemical suppliers.

Solid Supports

Although the Chromosorb materials, which are diatomaceous earth in origin, are commonly used supports in GLC work, Newman and Prausnitz[6,7,8] have indicated that columns prepared with these materials often give strongly asymmetric chromatogram peaks with highly polar solutes. Newman and Prausnitz also reported that interaction between a Chromosorb and polar solutes causes strong dependence of retention volume on sample size. Newman and Prausnitz showed, however, that retention volume of the polar solute acetonitrile, using several different polymer coating thicknesses, is independent of sample size using a Fluoropak column. Cheng and Bonner[12] pointed out that retention volume of benzene in PEO at 101.6°C is highly flow-rate dependent using Chromosorb P, but much less so using Fluoropak-80 (F-80). For these reasons, F-80 (a powdered Teflon) has been selected as the solid support material for our work.

Column Preparation

Columns of PEO-coated Fluoropak are prepared by first dissolving a weighed sample of PEO in chloroform and then stirring the solution with a weighed amount of solid support (F-80, 60/80 mesh). High shear is avoided in the mixing process of coating PEO onto F-80. The mixture is dried in the atmosphere for 5 to 15 hr, being stirred as long as possible to ensure a uni-

TABLE I
Chromatographic Columns[a]

Column no.	Original PEO weight,[b] g	F-80 support, g	Per cent loading
A	0.9912	11.6362	7.85
B	1.7908	13.0942	12.03
C	4.5107	11.7055	27.82
D	1.6571	10.9367	13.1583
E	3.5368	10.2365	35.6784
F[c]	0.8295	9.5907	8.2091
G	2.3640	9.9573	19.1862
I	0.7550	11.9814	5.9282
J	1.7553	10.4391	14.3942
K	2.3915	10.1093	19.1306
M	1.221	9.5902	11.2937
N	0.9931	9.7776	9.2204
Z	0	10.1	0
┌VI	1.00	14.59	6.41
│ XII	1.734	13.177	11.63
│ IX[d]	2.115	11.977	15
	poly(vinyl acetate)	Chromosorb	
│ XX	1.3527	14.2603	8.13
└XV	2.755	13.385	17.05

[a] All columns are 5 ft long (stainless steel or copper), ¼ in. o.d.

[b] During drying, columns C, D, E, G, I, J, K lost about ¼ of the weight of PEO listed above. Similarly, columns VI, XII, XX, and XV lost about ½ of the weights listed above.

[c] Made by Cheng (private communication) during this work.

[d] Made by Cheng (private communication) during this work.

form mixture. The mixture is then put in the drying oven, being taken out and weighed periodically until a nearly constant weight is reached. At this time, the chloroform is almost completely evaporated (at this time, chloroform odor is absent). Usually, the weight remains constant within 0.5% of the original PEO + F-80 weight for about 10 min and then decreases. About 5 ft of ¼-in.-o.d. tubing (stainless steel or copper) is filled, by vibration, with this mixture. The filled tubing is coiled to conform to the shape of the chromatographic oven. The characteristics of the GLC columns used in this study are summarized in Table I.

Test of the Apparatus

The apparatus has been tested by measuring the infinite-dilution specific retention volume (V_g^0), defined later, of benzene and toluene in poly(vinyl acetate) coated on Chromosorb P (column XV) at 100°C. The fit of the results deviates no more than 0.5% from those of Newman and Prausnitz.[7]

RESULTS

Data Reduction

We have obtained almost symmetric chromatogram peaks using F-80 as a support. Conder[15] pointed out that symmetric peaks are not necessarily a

guarantee that no adsorption is occurring on the polymer or uncoated support. Based on the work of Conder,[16] the observed solute retention volume is given by

$$V_N = K_L V_L + K_I A_I + K_S A_S \qquad (1)$$

where V_N = observed retention volume, V_L = volume of liquid phase, K_L = distribution coefficient for bulk solution, A_I = surface area of polymer, K_I = distribution coefficient for surface adsorption on the polymer, A_S = surface area of uncoated support, and K_S = distribution coefficient for surface adsorption on the uncoated support.

Dividing eq. (1) by V_L and taking the limit as V_L increases without bound gives

$$\lim_{V_L \to \infty} \frac{V_N}{V_L} = K_L. \qquad (2)$$

The value of K_L is independent of solute adsorption on the polymer or of solute adsorption on the uncoated support surface. Retention volume data V_g^0, defined later, obtained using a series of columns composed of different amounts of polymer coated on substrate are plotted according to eq. (2).

The retention volume per gram of polymer is related to K_L by

$$V_g = \frac{K_L}{\rho_L} \qquad (3)$$

where ρ_L is the polymer density. The specific retention volume corrected to 0°C is obtained from the relation[4]

$$V_g^0 = Q(t_q - t_r)\frac{273.2}{T}\frac{1}{m_2}f_p \qquad (4)$$

where V_g^0 = specific retention volume corrected to 0°C, Q = carrier gas flow rate measured at column outlet at temperature T, t_q = residence time of solute (measured to peak maximum), t_r = residence time of air (measured to peak maximum), m_2 = mass of polymer coated on the column, and f_p = pressure drop correction factor so that V_g^0 is corrected to average column pressure.

Based on the work of Purnell,[17] f_p is given by

$$f_p = \frac{3}{2}\frac{[(P_i/P_0)^2 - 1]}{[(P_i/P_0)^3 - 1]} \qquad (4')$$

where P_i = inlet pressure and P_0 = outlet pressure. As we shall see below, where weight loss of polymer occurs during column preparation or experimental operation, the term m_2 in eq. (4) must be modified by multiplying the original polymer weight m_2^0 by a term $(1 - x)$, where x is the fractional weight loss of polymer.

Flow Rate and Solute Injection Size Effect

We have determined the flow-rate dependence of the specific retention volumes of both polar and nonpolar solutes in PEO at 70°C. Solutes tested were acetone, methanol, benzene, methyl ethyl ketone, water, and n-butanol.

The flow-rate dependence of V_g^0 for these solutes is found to be so weak that we may assume V_g^0 to be independent of flow rate for both polar and nonpolar solutes in PEO.

We have also determined the dependence of specific retention volume of acetone, methanol, benzene, methyl ethyl ketone, water, and n-butanol in PEO on injected solute sample size at 70°C. Since sample size is proportional to chromatogram peak height, we used peak height as a measure of sample size. The sample size dependence of V_g^0 for these solutes is found to be so weak that we may assume V_g^0 to be independent of sample size for both polar and nonpolar solutes in PEO.

Effect of PEO Weight Loss on Results

We have found that significant PEO weight loss can occur during column preparation. Figure 2 shows V_g^0 for benzene at 75°C versus $1/V_L$ for columns A, B, and N prepared using our standard column preparation procedure. The coverage ratios (weight of PEO/weight of F-80) of columns A, N, and B are 0.085, 0.102, and 0.137, respectively. Higher coverage ratios were not used for columns prepared by our standard method because, for coverage ratios higher than approximately 0.14, the PEO + F-80 mixtures form aggregates of unevenly coated particles after drying to nearly constant weight. Newman and Prausnitz[6] have shown in their work with polystyrene that if the coverage ratio is above 0.15, surface adsorption effects are usually negligible. As shown in Figure 2, the benzene results for columns A, B, and N are essentially identical. Since the coverage ratio for column B is nearly 0.15 and the results of columns N and B are nearly identical, we therefore assume that the results for column N are independent of surface adsorption effects. The reliability of this assumption will be tested by comparing the results obtained from column N and those obtained from column C, which has a coverage ratio of about 0.40. To avoid aggregation of particles and obtain higher coverage
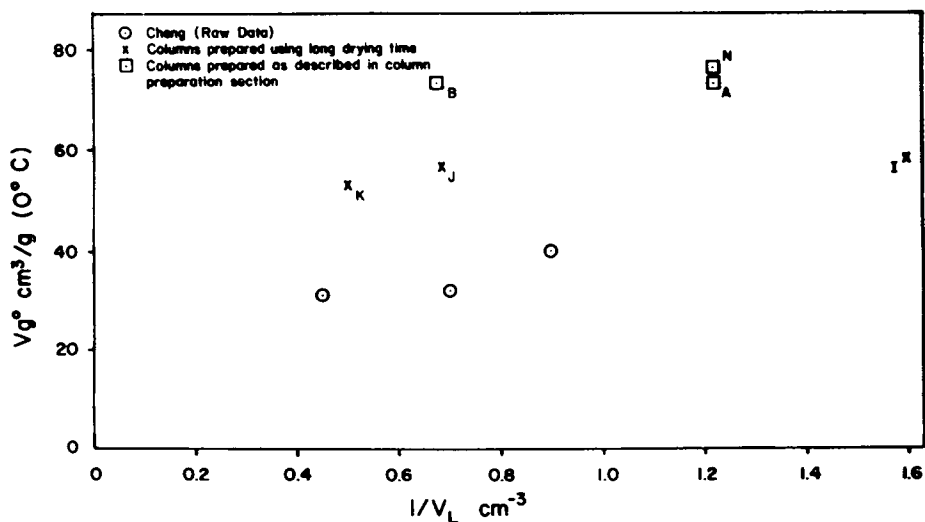

Fig. 2. Apparent retention volume of benzene in PEO at 75°C (uncorrected for PEO weight loss).

ratio columns, one may consider putting the PEO + F-80 mixture in the drying oven for a longer time. The only weight loss in the drying oven after chloroform evaporation is PEO weight loss. However, all columns (except columns A, B, and N) prepared using longer drying times give retention volumes less than those obtained using columns A, B, and N, as shown in Figure 2 for 75°C. Results obtained at 102°C are similar. This is probably due to PEO weight loss by depolymerization, since traces of liquid-phase degraded material (probably low molecular weight PEO) can be found after long drying times. Raw data (uncorrected for PEO weight loss) obtained by Cheng and Bonner[12] in the early stages of their work are also shown in Figure 2. The much smaller values of V_g^0 obtained by Cheng and Bonner in their work are due to the fact that much longer oven-drying times were used, so their columns experienced considerable PEO degradation. The values of PEO weight and loading ratio listed in Table I have not been corrected for PEO weight loss.

We have also found that PEO weight loss occurs during experimental runs, as shown in Table II. Table II shows the history of each chromatographic column.

The amount of PEO weight loss must be taken into account in the data reduction. Since the weight of PEO coated on the substrate in a column is not a constant, eq. (4) is modified to account for polymer weight loss due to polymer degradation:

$$V_g^0 = Q(t_q - t_r)\frac{273.2}{T}\frac{1}{m_2^0(1 - x)}f_p \tag{5}$$

where x = fractional weight loss of polymer in the column, and m_2^0 = original weight of polymer. As soon as prepared, a column is put in the GLC apparatus to obtain the first reference value of V_g^0, based on m_2^0; 70°C is arbitrarily chosen as the first reference temperature because it is above the melting point (65° ± 2°C) and PEO degradation is not significant at 70°C. We assume $x = 0$ between the time of column preparation and the time the first reference datum is taken. Based on the first value of V_g^0 and the value of m_2^0, x can be estimated as follows: If $x \neq 0$, then taking x into account gives

$$V_g^0 = Q(t_q - t_r)\frac{273.2}{T}\frac{f_p}{m_2^0(1 - x)} = \text{true value.} \tag{6}$$

Not taking x into account gives

$$V_g^{0\prime} = Q(t_q - t_r)\frac{273.2}{T}\frac{f_p}{m_2^0} = \text{apparent value.} \tag{7}$$

Dividing eq. (7) by (6) gives

$$1 - x = \frac{V_g^{0\prime}}{V_g^0} \tag{8}$$

or

$$x = \frac{V_g^0 - V_g^{0\prime}}{V_g^0} \tag{9}$$

TABLE II
History of Each Column

Column no.	Weight PEO after oven drying, g	Original loading, %	History and V_g^0 reduction, %, due to weight loss	Solute used to measure V_g^0
A	0.9912	7.85	finite run with benzene temperature greater than boiling; 100%	benzene
B	1.7908	12.03	finite run with benzene temperature greater than boiling; 100%	benzene
C	4.5107	27.82	1. infinite run, 150°C, 15 solutes 1 day; 3.7% 2. infinite run, 102°C, 15 solutes 1 day; 0.2% 3. infinite run, 88°C, 15 solutes 1 day; 0% 4. infinite run, 70°C, 15 solutes 1 day; 0% 5. infinite run, 70°C → 88°C → 125°C (15 solutes) → 150°C (15 solutes) → 102°C (15 solutes) → 88°C (15 solutes) → 70°C (15 solutes) → 150°C (100 μl H$_2$O) → 70°C (benzene only), 7 days; 10.4%	benzene
D	1.6571	13.1583	1. finite run, 120°C & 70°C, 7 days; 13.3% 2. infinite run, 70°C → 120°C → 125°C → 150°C → 88°C → 70°C, benzene only, 2 days; 8%	benzene
E	3.5368	25.6784	infinite run, 70°C → 88°C → 102°C → 125°C → 150°C → 70°C, benzene only, 3 days; 3.5%	benzene
F	0.8295	8.2091	not determined	
G	2.3640	19.1862	1. infinite run, 70°C → 88°C → 102°C → 125°C → 150°C → 125°C → 102°C → 88°C → 70°C, 1 solute, 4 days; 6.5% 2. infinite run, 70°C, 1 solute 3 days; 4.16%	benzene
I	0.7550	5.9282	infinite run, 70°C → 75°C → 88°C → 102°C → 125°C → 150°C → 70°C, 1 solute, 2 days; 11.85%	benzene
J	1.7653	14.3942	not determined	
K	2.3915	19.1306	infinite run, 70°C → 75°C → 88°C → 102°C → 125°C → 150°C → 70°C, 1 solute, 2 days; 12.82%	benzene
M	1.221	11.2937	not determined	

(*Continued*)

TABLE II (*Continued*)

Column no.	Weight PEO after oven drying, g	Original loading, %	History and V_g^0 reduction, %, due to weight loss	Solute used to measure V_g^0
N	0.9931	9.2204	1. infinite run, 70°C, 15 solutes, 1 day; 0%	
			2. infinite run, 75°C, 15 solutes, 1 day; 1.3%	
			3. infinite run, 88°C, 15 solutes, 1 day; 0%	
			4. infinite run, 102°C, 15 solutes, 1 day; 1.2%	
			5. infinite run, 125°C, 15 solutes, 1 day; 2.6%	
			6. infinite run, 150°C, 15 solutes, 1 day; 3.4%	
			7. total infinite run, 70°C → 75°C → 88°C → 102°C → 125°C → 150°C, 15 solutes, 5 days;	
			a. 9.6%	benzene
			b. 9.5%	toluene
			c. 7.2%	acetone
			d. 15.3%	MEK
			8. finite run, 70°C → 125°C, 8 days; 1.4%	benzene
			9. finite run, 150°C, 1 day; 0%	benzene
			10. finite run, 125°C, 1 day; 4.67%	benzene
			11. finite run, 88°C → 75°C, 2 days; 0%	benzene
Z	0	0	0%	
VI	1.00	6.41	1. stored at room temperature, 7 months; 45%	benzene
			2. stored at room temperature, 9½ months; 60%	
XII	1.734	11.63	stored at room temperature, 7 months;	
			a. 24%	benzene
			b. 17%	*n*-butanol
			c. 26%	toluene
IX	2.115 poly(vinyl acetate)	15 Chromosorb	stored at room temperature, 7 months; 0%	
XX	1.3527		stored at room temperature, 7 months;	
			a. 20%	benzene
			b. 22%	*n*-butanol
XV	2.755		stored at room temperature, 7 months; 20%	benzene

where the true value of V_g^0 is equal to that of the first reference value of V_g^0 at constant temperature. In order to determine x as accurately as possible, and also to minimize changes in x due to changes in system temperature, we obtained V_g^0 of 15 solutes at each temperature within one day and completed within one week all isotherms between 70°C → 150°C → 70°C and the
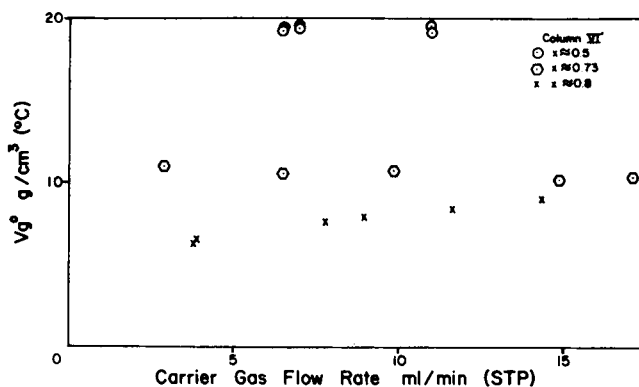
Fig. 3. Flow rate dependence of benzene retention volume in PEO at 101.6°C for different degrees of PEO degradation.

TABLE III

Specific Retention Volumes of Solutes in Polyethylene Oxide WSR-301[a]

| | $V_g{}^0$ (at 0°C), cm³/g | | | | | |
Solute	70.2°C	75.2°C	88.2°C	101.9°C	125.7°C	150.5°C
Water	283.93	219.66	131.0	67.86	31.49	15.74
Methanol	93.03	76.22	44.35	26.75	14.27	8.15
1-Butanol	431.59	334.56	194.15	114.16	53.69	26.4
Carbon tetrachloride	50.84	41.92	30.41	21.21	13.14	7.49
Chloroform	124.03	102.6	67.58	43.91	23.69	12.74
1,2-Dichloroethane	189.85	155.18	101.43	64.38	33.83	18.77
1,1,2-Trichloroethane	643.16	523.57	316.54	186.14	88.64	42.0
Benzene	89.36	76.12	50.95	35.09	20.33	11.99
Toluene	173.61	145.25	97.52	62.71	33.49	18.68
o-Xylene	430.53	356.61	228.0	142.68	72.59	36.3
Acetone	50.42	42.86	28.84	21.31	12.53	7.553
Methyl ethyl ketone	86.70	74.11	48.68	32.91	18.44	10.56
Tetrahydrofuran	66.24	58.27	38.12	26.53	14.76	9.27
Acetonitrile	164.11	135.75	90.88	55.74	31.48	15.88
Butyl acetate	246.01	202.52	128.37	80.59	41.36	21.02

[a] Results obtained using column N. Conditions: flow rate, 18.33 cm³/min (S.T.P.); injection amount, 0.5—1.0 μl.

TABLE IV

Comparison of Acetone $V_g{}^0$ of Column N, Column C, and Cheng and Bonner's Work

T, °C	Column N[a]	Column C[b]	Cheng and Bonner[c]
70	50.42	56.07	
75	42.86		80.3
88	28.84	33.5	57.5
102	21.31	23.57	
125	12.53	14.73	21.8
150	7.553	8.65	11.5

[a] x about 0—0.1.
[b] x about 0.3—0.37.
[c] x about 0.5—0.6.

TABLE V
Comparison of Toluene V_g^0 of Column N, Column C, and Cheng and Bonner's Work

T, °C	Column N[a]	Column C[b]	Cheng and Bonner[c]
70	173.61	173.5	
75	145.25		143
88	97.52	92.02	90.4
102	62.71	61.8	66.8
125	33.49	33.45	34.0
150	18.68	16.35	17.4

[a] x about 0—0.1.
[b] x about 0.3—0.37.
[c] x about 0.5—0.6.

change of each x value at each temperature run to ensure that changes in x during temperature changes between runs are properly accounted for.

In Figure 3, V_g^0 of benzene in PEO versus flow rate obtained from column VI′ is shown for several values of x. Column VI′ had $x = 0.5$ when it was prepared. Column VI′ had $x = 0.73$ about 7 months after preparation and $x =$
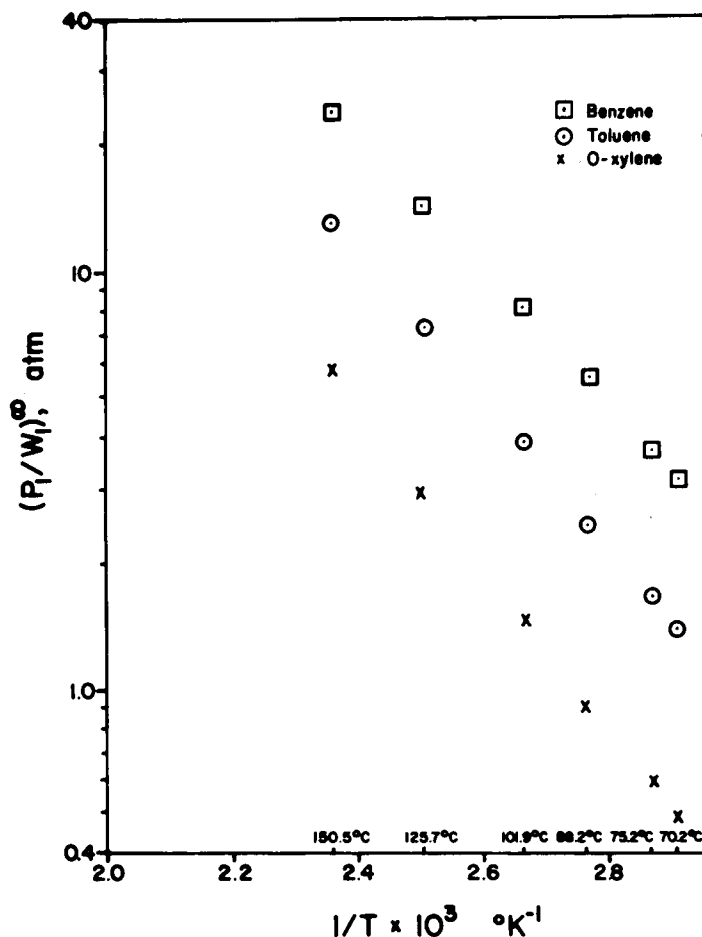
Fig. 4. Infinite-dilution volatilities of benzene, toluene, and o-xylene in PEO.
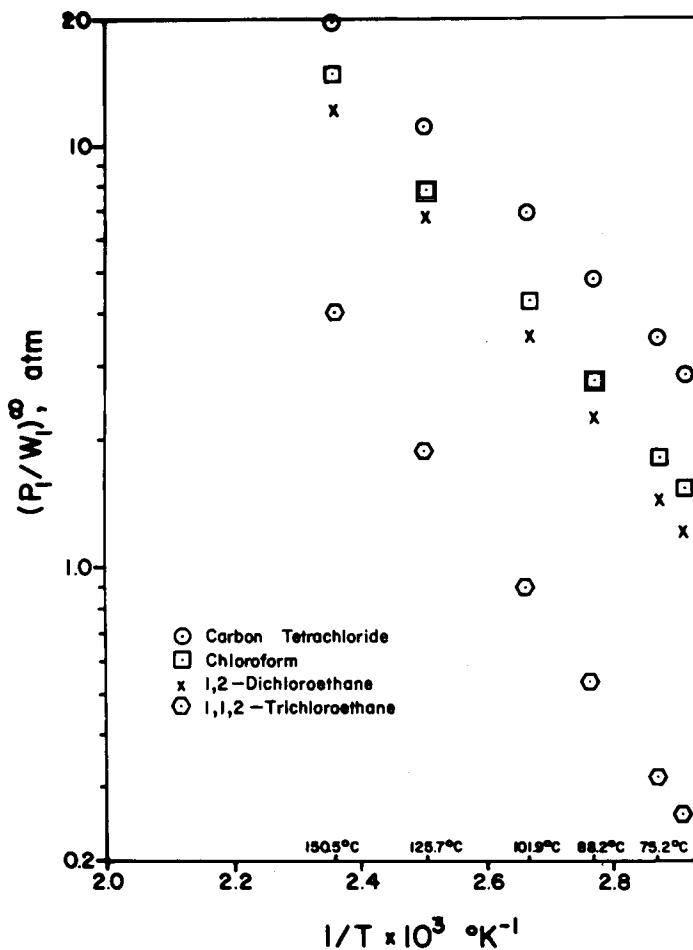
Fig. 5. Infinite-dilution volatilities of carbon tetrachloride, chloroform, 1,2-dichloroethane, and 1,1,2-trichloroethane in PEO.

0.8 about 9.5 months later. It is worthwhile to note that V_g^0 of benzene is almost independent of flow rate when x is below 0.73 but is strongly flow-rate dependent when x is 0.8. In the work of Cheng and Bonner,[12] the columns used have $x = 0.5$, as shown in Figure 2. Cheng and Bonner have determined that V_g^0 of polar solutes such as acetone in PEO is strongly flow-rate dependent. We have found, however, that V_g^0 values of polar solutes obtained from column N (which has $x = 0$) are almost independent of flow rate and solute sample size. Therefore, GLC columns using PEO apparently change characteristics when PEO degradation is severe.

DISCUSSION OF RESULTS

Retention volumes for several solutes, obtained using column N at temperatures from 70.2° to 150.5°C are presented in Table III. In Tables IV and V, we have compared the results obtained using column N, which had a coverage ratio of 0.085 and $x = 0$ originally, with those obtained using column C, which
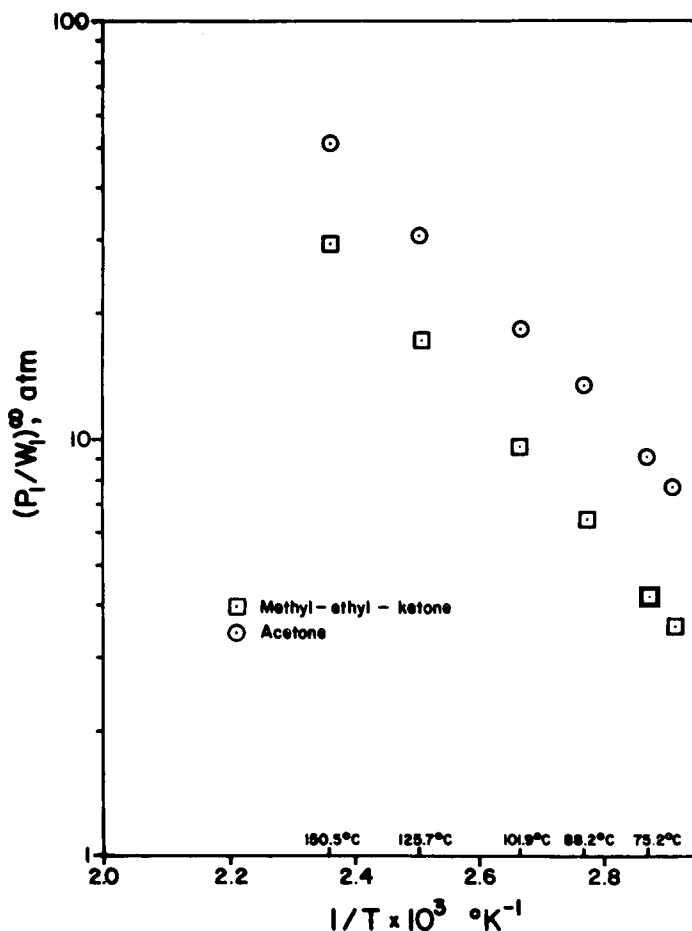
Fig. 6. Infinite-dilution volatilities of methyl ethyl ketone (MEK) and acetone in PEO.

had a coverage ratio of about 0.4 and $x = 0.3$ originally. Table IV gives a comparison between the results for acetone obtained in this work using columns N and C and the published results of Cheng and Bonner.[12] Table V shows a similar comparison for toluene. Although not shown, the comparison of the type given in Table V for toluene is qualitatively similar to the results for benzene.

From the above discussions, we believe that the difference between the results of columns N and C is mainly due to differences in x rather than differences in coverage ratios, flow rates, or solute sample sizes. Therefore, the results obtained from column N are assumed to be relatively accurate. From Tables IV and V, it is worthwhile to note that even though the values of x and coverage ratio for columns N and C are different, the results for toluene are identical, within GLC experimental error. However, the results for polar solutes such as acetone show deviations which are larger than experimental error.

As shown in Figure 2, the columns used by Cheng and Bonner[12] have $x = 0.5$. We believe that their results for polar solutes deviate more than those of
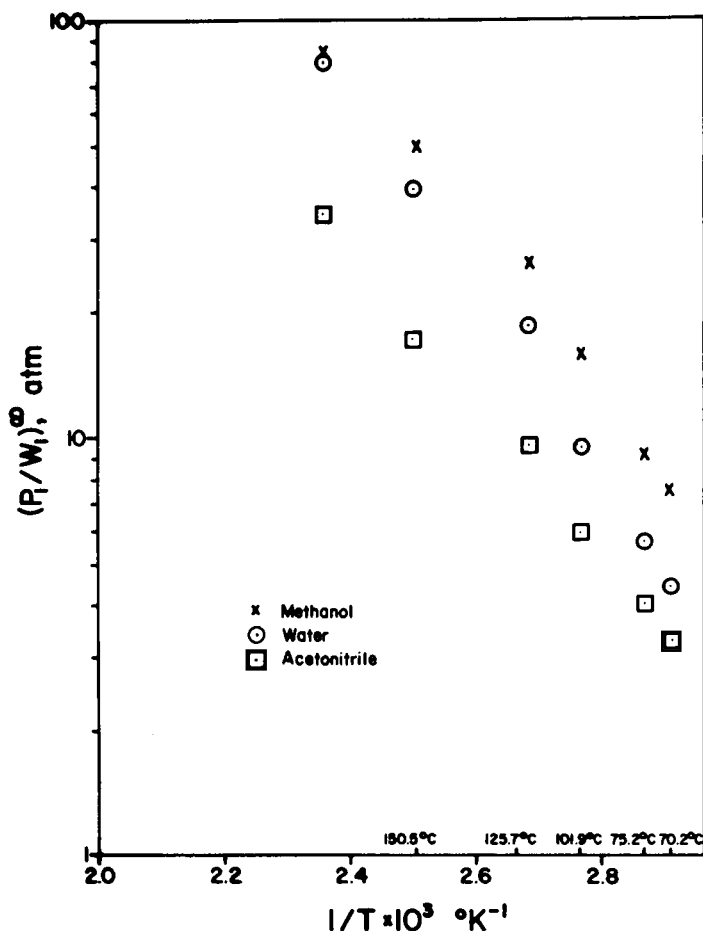
Fig. 7. Infinite-dilution volatilities of methanol, water, and acetonitrile in PEO.

column C when compared to the results of column N because of their larger x values. Table IV shows this comparison for the polar solute acetone.

From Table IV, it is seen that the discrepancy is probably due to larger x and not due to different coverage ratios. The comparison for nonpolar solute toluene is shown in Table V. Table V shows essentially similar results. It should also be noted that changes in x during experimental runs were accounted for in analyzing data from column N, while Cheng and Bonner[12] did not do so.

At modest total pressure, the weight-fraction activity coefficient of a non-polar solute at infinite dilution is[4]

$$\ln\Omega_1^{\infty} = \ln\left(\frac{a_1}{w_1}\right)^{\infty} = \ln\left[\frac{273.2R}{P_1^{s}V_g^{0}M_1}\right] - \frac{P_1^{s}}{RT}(B_{11} - v_1) \qquad (10)$$

where $\Omega_1^{\infty} = \mathrm{Lim}_{w_1 \to 0}\,(a_1/w_1) = (a_1/w_1)^{\infty} =$ infinite-dilution activity coefficient based on weight fraction, $a_1 =$ activity of solute, $w_1 =$ weight fraction of solute, $R =$ gas constant, $P_1^{s} =$ saturation vapor pressure of solute at T, $T =$ column temperature, $M_1 =$ molecular weight of solute, $B_{11} =$ second virial
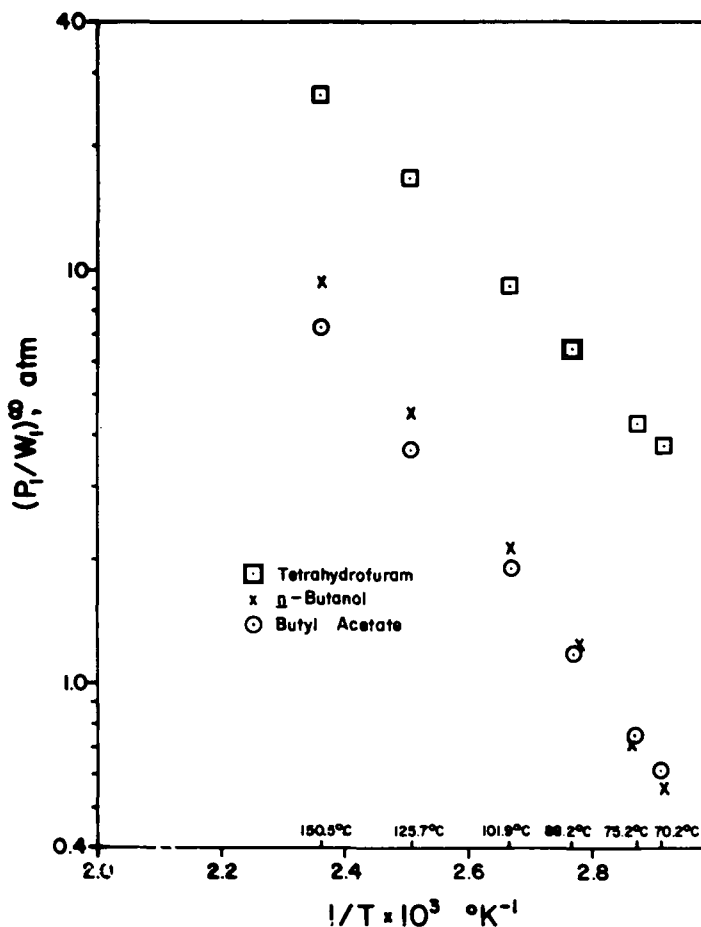
Fig. 8. Infinite-dilution volatilities of tetrahydrofuran, n-butanol, and butyl acetate in PEO.

coefficient of pure solute at T, and v_1 = solute molar volume at T. The standard state in eq. (10) is pure, liquid solute at system temperature and zero pressure. For convenience, we use a different standard state: pure, saturated liquid solute at system temperature. Equation (10) then becomes

$$\Omega_1^{\infty} = \left(\frac{a_1}{w_1}\right)^{\infty} = \frac{273.2R}{P_1^s V_g^0 M_1} \exp\left[(-P_1^s B_{11})/(RT)\right]. \qquad (11)$$

Newman and Prausnitz[6,7,8] derived a simple expression to interpret infinite-dilution data:

$$\left(\frac{P_1}{w_1}\right)^{\infty} = \frac{RT}{V_g^0 M_1} \qquad (12)$$

where $(P_1/w_1)^{\infty}$ = infinite-dilution volatility of the solute (Henry's constant). In the absence of solubility isotherms for concentrated polymer solutions, solute partial pressure can be approximated by

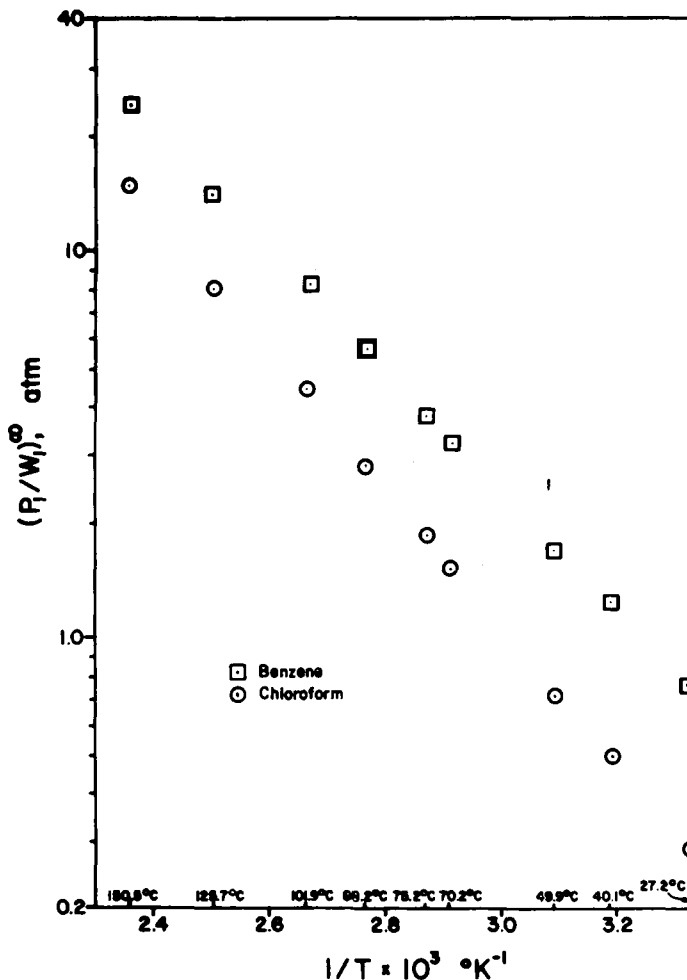$$P_1 = w_1 \left(\frac{P_1}{w_1}\right)^{\infty} \qquad (13)$$

Fig. 9. Infinite-dilution volatilities of benzene and chloroform in PEO.

at small solute concentrations with the assumption that Henry's law holds for the solute. As solute concentration increases, the reliability of eq. (13) diminishes rapidly. Results of $(P_1/w_1)^\infty$ versus $1/T$ are shown in Figures 4 to 9 for 14 organic solutes and water at temperatures from 70° to 150°C.

Interpretation of GLC Results

The infinite-dilution volatilities shown in Figures 4 to 9 can be used to calculate solute partial pressure over PEO solution up to several weight per cent by assuming Henry's law.

While the plots in Figures 4 to 9 are nearly straight lines, they should not be extrapolated below the PEO melting temperature (65° ± 2°C). In Figure 12, a slight discontinuity on the plots of log $(P_1/w_1)^\infty$ of benzene and chloroform versus $1/T$ occurred about 65°C, which is the melting temperature of PEO. Guillet[18] has attributed the discontinuity to changes in the per cent crystallinity of the polymer as the temperature passes through the melting range.

Test of GLC Results

Using the semiempirical method suggested by Bonner and Prausnitz,[19] we have extrapolated the "static" results of Booth and Devoy to infinite dilution. This gives a value of about 4 for Ω_1^∞ of benzene in PEO. We have measured V_g^0 for benzene at 70°C to be 89.36 cm^3/g. Applying eq. (11), we find a value of 4.57 for Ω_1^∞. There are several possible reasons for this slight discrepancy. One explanation is that one or both values of the infinite-dilution activity coefficient are in error because 70°C is close to the melting temperature of PEO. Another explanation is incorrect determination of x, for example, change in x between the time of column preparation and the time the first datum is obtained. The third explanation is that the GLC data are in fact not the same as those obtained by static methods for $(a_1/w_1)^\infty$ of benzene in PEO. However, the discrepancy is so slight that one may conclude that GLC and "static" techniques agree reasonably well.

CONCLUSIONS

The advantages of GLC to obtain infinite-dilution data are that data reduction, eq. (4), requires very little computation and that the measurements are simple and rapid and require only standard equipment. However, x in eq. (6) should be carefully determined, otherwise large errors may occur.

The changing of PEO solution characteristics due to PEO degradation has been discussed and taken into account in our GLC results which have been presented for water and 14 organic solutes at temperatures from 70° to 150°C. The discrepancy between our results and those of Cheng and Bonner[12] is mainly ascribed to changing characteristics of the columns when x is large.

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