tween enthalpy parameters obtained by the methods of glc and vapor sorption are limited to only a few cases. One other system for which comparable data are available is natural rubber and benzene. In this case, the glc value[4] of κ_S is +0.18, while $\kappa_S = 0.01 \pm 0.1$ has been obtained by vapor sorption.[11] It appears from the somewhat sparse data collected to date that estimates of the residual enthalpy obtained by glc methods are as reliable as those obtained by static methods. Corrections for gas phase imperfection must be very carefully applied.

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Sorption of Solutes by Poly(ethylene oxide) Using Gas–Liquid Chromatography

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ABSTRACT: We have used gas–liquid chromatography (glc) to study equilibrium sorption by poly(ethylene oxide) (PEO) of small amounts of 12 organic solutes between 50 and 150° at essentially atmospheric pressure. Solute specific retention volumes and infinite-dilution volatilities are presented and discussed. Comparison of glc and static results for benzene sorption shows fair agreement between the data obtained using the two methods.

Poly(ethylene oxide) (PEO) is a commercially important, water-soluble polymer which is used in formulation of adhesives, pharmaceuticals, cosmetics, water-soluble packaging films, paper coatings, textile warp sizes, and friction-reducing additives. In some of these applications, the PEO is applied to a surface as a thin layer of concentrated solution and then dried to form a thin, water-soluble film. In order to understand the drying process more fully, we have studied sorption of small amounts of several organic solvents and water in PEO from 50 to 150°.

The experimental technique we have used is gas–liquid chromatography (glc). Its use in determining the activities of solvents in polymers was originally proposed by Smidsrød and Guillet[1] and described in detail by Newman and Prausnitz.[2,3]

Experimental Section

Apparatus and Procedure. The gas chromatograph used is an F & M 500 equipped with a thermal conductivity detector. The column oven was rebuilt, and oven temperature was controlled to ±0.1° by a Hallikainen Thermotrol. The carrier gas was helium, and its flow rate was controlled by a Negretti and Zambra precision regulator. Carrier gas flow rate was measured with a soap-bubble flowmeter. Carrier gas flow rate was measured to ±0.2 ml/min (at STP). Inlet and outlet column pressures were read to ±0.1 mm with two mercury manometers. Liquid samples were injected into the flowing helium stream through a silicone rubber septum with a 1 μl Hamilton syringe. The reliability of the apparatus was tested by reproducing, within experimental error, the data of Newman and Prausnitz[4] for poly(vinyl acetate) with various solutes.

Preparation of Columns. Two column packing materials were tested for use as PEO substrates: Chromosorb P (AW-DMCS) and Fluoropak-80, both 60–80 mesh. Columns were prepared by mixing a dilute solution of PEO in chloroform with substrate and evaporating to constant weight by heating. The coated support was packed into 5 ft of 0.25-in. stainless-steel tubing which was subsequently coiled to conform to the shape of the chromatograph oven. Unless care was taken to remove all but traces of water from the chloroform and air in the drying oven, some PEO was lost by depolymerization.

Column Support Materials. Chromosorb P (AW-DMCS) and Fluoropak 80 were tested as support materials. Our data indicate that specific retention volume Vg (defined later) was highly flow-rate dependent using Chromosorb P but much less so using Fluoropak 80. In addition, the solute chromatogram peaks were highly asymmetric using Chromosorb P but nearly symmetric using Fluoropak 80. For these reasons, we selected Fluoropak 80 as the support material to be used for this study.

Stationary Phase and Solutes. The PEO was WSR-301 "Polyox" supplied by the Union Carbide Corp., having a viscosity-average molecular weight of 4×10^6 g/g-mol, a melting range of 65 ± 2°, and a density of 1.21 g/cm^3 (determined by Union Carbide) at 25°.

The solutes were reagent grade materials supplied by various chemical suppliers.

Data Reduction. The state of aggregation of polymer coated material in a glc column is quite different from that of bulk polymer. According to Conder, *et al.*,[5] the observed retention volume is given by

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

where V_N = retention volume, V_L = volume of the liquid phase, K_L = distribution coefficient for the bulk solution, K_S = distribution coefficient for the surface adsorption, A_S = surface area of the

Table I
Chromatographic Columns[a]

Column no.	Weight, g PEO	Weight, g Support	$1/V_L$, cm^{-3} (25°)	Support type
VI′	0.315	14.59	3.84	FP80
X	0.523	23.942	2.31	FP80
XII	0.708	13.177	1.71	FP80
XV	1.07	13.385	1.13	FP80
XX	0.690	14.260	1.75	FP80
N	0.993	9.778	1.22	FP80

[a] All columns were 5 ft long, 0.25 in. i.d., 316 SS.

uncoated support, and A_I = surface area of the polymer. Dividing (1) by V_L and taking the limit as V_L becomes large, one has

$$\lim_{V_L \to \infty} (V_N/V_L) = K_L \tag{2}$$

which is the true solution result, independent of solute adsorption on the uncoated support or on the polymer surface.

In order to determine the true thermodynamic solubility of a solute in the polymer, one must obtain chromatographic data for several columns coated with different amounts of polymer and extrapolate the results to large V_L ("infinite loading"). For convenience, we have chosen to represent our results as specific retention volume V_g, which is related to K_L by

$$V_g = K_L/\rho_L = V_N/\rho_L V_L \tag{3}$$

where ρ_L is the polymer density. Specific retention volume V_g is obtained from the relation (Newman and Prausnitz[3])

$$V_g = Q(t_g - t_r)(f_p/m_2) \tag{4}$$

where Q = carrier gas flow rate measured at the column outlet, m_2 = mass of polymer coated on the column, t_g = time required for air to pass through the column (measured to peak maximum), and t_r = time required for solute to pass through the column (measured to peak maximum). There is a pressure drop across the column, so V_g is corrected to the average column pressure by the factor f_p (Purnell[6])

$$f_p = \frac{3}{2}\frac{[(p_i/p_o)^2 - 1]}{[(p_i/p_o)^3 - 1]} \tag{5}$$

where p_i = pressure at the column inlet, and p_o = pressure at the column outlet.

Six columns of different PEO loadings were used in this study and are listed in Table I.

To ensure that the data for each column represent equilibrium as nearly as possible, the data for each solute were obtained at several different helium carrier gas flow rates (ranging from 10 cm^3/min to approximately 1 cm^3/min) and extrapolated to zero flow rate prior to extrapolation to infinite loading ($V_L \to \infty$).

We noted during the experiments that it was possible to lose some of the PEO in the columns by depolymerization between the time of making the column and the time of its use. As the elapsed period between column manufacture and use (or reuse) was sometimes several days, we needed to correct for any PEO weight loss in the columns. As weighing and reweighing each column to determine weight loss is usually inaccurate, we used another method of making such a correction. Using columns immediately after manufacture gave reproducible results which indicated that the specific retention volume of benzene at 70° is independent of flow rate and column loading, within experimental precision. Thus if any PEO were lost due to depolymerization, the corresponding decrease in the specific retention volume of benzene at 70°, measured at any convenient flow rate, could be used to determine the weight of PEO remaining coated on the Fluoropak. In order to determine precisely the weight of PEO on each column before each run, we measured the specific retention volume at 70° for that column. The correct weight of PEO in the column is given by the original weight of PEO (V_g^0(measured)/V_g^0(correct)).

We express all retention volumes at 0°; such standard retention volumes are denoted V_g^0. The dependence of V_g^0 on column loading is linear for most solutes we have tested. In the extrapolation of V_g^0 to infinite loading, we used a constant density of 1.21 g/cm^3 to calculate V_L rather than the density corresponding to each temperature. This procedure does not change the limiting value of V_g^0, because extrapolating V_g^0 *vs.* $1/V_L$ to $1/V_L = 0$ using a constant density is identical to extrapolating V_N/V_L *vs.* $1/V_L$ using the correct density at each temperature. We estimate the reproducibility of the retention volumes at each loading to be better than ±5%.

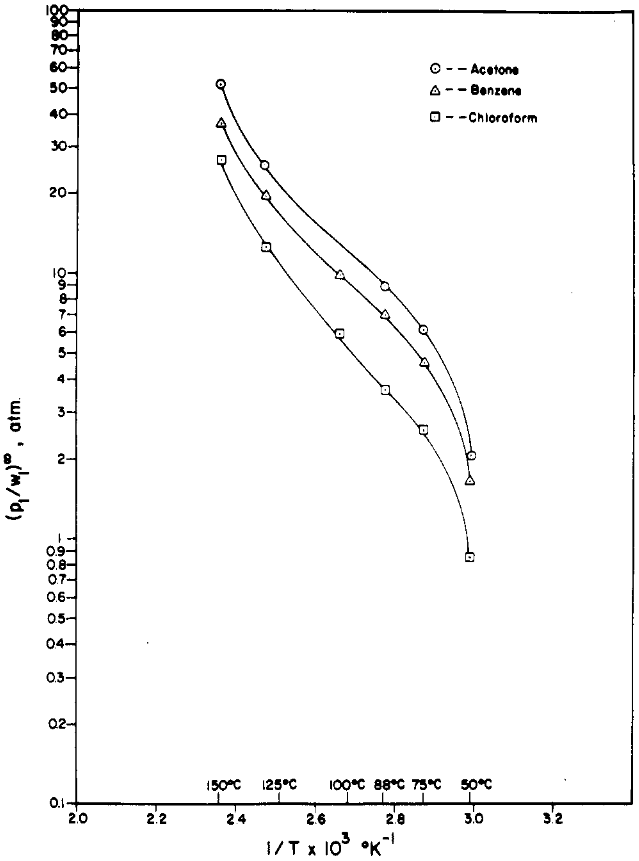

Figure 1. Infinite-dilution volatilities in PEO.

Solute retention volumes, extrapolated to infinite loading, are listed in Table II.

Discussion of Results

In order to interpret our data, we have calculated the quantity $(p_1/w_1)^\infty$, which is the limit of the solute partial pressure divided by the solute weight fraction as the solute weight fraction approaches zero. After Newman and Prausnitz,[3] we shall refer to this quantity as the "infinite-dilution volatility." The infinite-dilution volatility is given by

$$(p_1/w_1)^\infty = RT/(V_g M_1) \tag{6}$$

Infinite-dilution volatility results are listed in Table III.

In the absence of isotherms of solute partial pressure as a function of solute concentration, infinite-dilution volatility can be used to make an estimate of solute partial pressure at finite concentration by assuming behavior based on Henry's law. At small, finite solute concentrations, solute partial pressure can be approximated by

$$p_1 = w_1(p_1/w_1)^\infty \tag{7}$$

The reliability of eq 7 diminishes rapidly as concentration approaches a few weight per cent solute.

Typical infinite-dilution volatility results are plotted in Figure 1. Several of the curves presented in Figure 1 might have been approximated by straight lines determined by linear regression. However, in most cases the deviation between the straight-line regression fit and the data is signifi-

Table II
Specific Retention Volumes[a] of Solutes in Poly(ethylene oxide)

	V_g^0, cm^3/g					
Solute	50°	75°	88°	101.6°	125°	150°
Carbon tetrachloride	89.5	43.5	38.2	26.5	13.8	5.2
Chloroform	261	93.8	68	43.5	21.5	10.8
1,1-Dichloroethylene	164	61.5	40.0	31.0	16.6	8.5
1,2-Dichloroethane	527	205	126	86.9	37.2	14.
1,1,1-Trichloroethane	1400	561	343	242	111	38.0
Benzene	210	79.0	63.7	40.0	21.3	12.1
Toluene	329	143	90.4	66.8	34.0	17.4
Acetone	213	80.3	57.5		21.8	11.5
Methyl ethyl ketone	313	111	69.2	47.0	21	0
Tetrahydrofuran	151	85.0	67.5	44.0	24.5	4.5
Acetonitrile	660	226	155	102	58.0	20.3
Butyl acetate	834	279	177		59.8	17.2

[a] At 0°, extrapolated to infinite loading.

Table III
Infinite Dilution Volatility of Solutes in Poly(ethylene oxide)

	$(p_1/w_1)^\infty$, atm					
Solute	50°	75°	88°	101.6°	125°	150°
Carbon tetrachloride	1.93	4.27	5.04	7.54	15.4	43.4
Chloroform	0.851	2.55	3.65	5.92	12.7	26.9
1,1-Dichloroethylene	1.67	4.79	7.64	10.2	20.3	42.1
1,2-Dichloroethane	0.508	1.41	2.38	3.58	8.88	25
1,1,1-Trichloroethane	0.142	0.382	0.648	0.952	2.21	6.85
Benzene	1.62	4.63	5.96	9.84	19.6	36.7
Toluene	0.875	2.17	3.56	5.00	10.4	21.7
Acetone	2.14	6.13	8.88		25.8	52.0
Methyl ethyl ketone	1.18	3.57	5.94	9.08	21.6	
Tetrahydrofuran	2.44	4.66	6.09	9.69	18.5	110
Acetonitrile	0.979	3.08	4.66	7.34	13.7	41.7
Butyl acetate	0.274	0.882	1.44		4.71	17.4

cantly greater than the estimated experimental error, indicating that the curvature shown is probably not an artefact of the data. Several trends are evident from the curves in Figure 1. Since the melting temperature of PEO is approximately 65°, the plots of ln (p_1/w_1) *vs.* $1/T$ are nonlinear between 50 and 75°. Guillet[7] has attributed the nonlinearity to changes in the per cent crystallinity of the polymer as the temperature passes through the melting range.

The benzene and chloroform curves approach linearity at temperatures greater than the melting temperature, as expected (see Newman and Prausnitz[3]). Compounds which can form hydrogen bonds with the PEO, such as acetone, deviate from linearity at high temperatures, probably because hydrogen bonding diminishes as temperature increases. At the higher temperatures, 125 and 150°, the infinite-dilution volatility of the hydrogen-bonding solutes increases because hydrogen bonding with PEO, which enhances solubility, has diminished.

Comparison with Other Workers

The only data with which we can directly compare our results are those of Booth and Devoy,[8] who have reported activity coefficients of benzene in PEO at 70°. In order to compare our data with those of Booth and Devoy, we must calculate the infinite-dilution activity coefficient of benzene in PEO. Solute activity coefficients in polymers can be obtained from glc data at temperatures greater than the polymer glass transition temperature (Smidsrφd and Guillet[1]). The glass transition temperature of PEO is 206K (Swallow[9]); our working temperature range is well above the glass transition temperature. At modest total pressures, the weight-fraction activity coefficient of a nonpolar solute, such as benzene, at infinite dilution is given by (Patterson and Guillet[10])

$$\Omega_1{}^\infty = (a_1/w_1)^\infty = (273.2R)/(p_1{}^sV_g{}^\circ M_1)\exp[(-p_1{}^sB_{11})/(RT)] \quad (8)$$

where a_1 = solute activity, w_1 = solute weight fraction in the polymer phase, R = gas constant, $p_1{}^s$ = solute vapor pressure at temperature T, $V_g{}^0$ = specific retention volume at 0°, M_1 = solute molecular weight, B_{11} = second virial coefficient of solute at temperature T, and T = absolute temperature. The standard state for eq 8 is pure, saturated solute at temperature T.

The results of Booth and Devoy were obtained at 70°. We have measured $V_g{}^0$ for benzene at 70° to be 92.95 cm^3/g. Applying eq 8 to our data, we find a value of 4.4 for $\Omega_1{}^\infty$.

Booth and Devoy[8] report data for two PEO fractions at 70°: 205F ($M_n = 6 \times 10^5$ g/g-mol) and 6000F (M_n = 5700 g/g-mol). The activity results for both fractions are virtually identical. However, the lowest weight fraction of benzene reported for fraction 205F is 0.0967, while results for fraction 6000F are given to a weight fraction of 0.0290. We have extrapolated the results of Booth and Devoy to infinite dilution using the semiempirical method suggested by Bonner and Prausnitz.[11] This gives a value of approximately 4 for $\Omega_1{}^\infty$. Thus, the two methods agree reasonably well, although there may be a slight discrepancy between the data obtained by the two methods.

While there is a discrepancy in the results which is slightly greater than the probable experimental error, it should be noted that there are several possible causes for this. One possible explanation is that the glc data are in fact not the same as those obtained by static methods for benzene/PEO. Another possible explanation is that one or both values of the infinite-dilution activity coefficient are in error because 70° is close to the melting temperature of

PEO, making reliable data difficult to obtain. Yet another possible cause of the very slight disagreement is the fact that the molecular weight of our PEO sample is much larger than those used by Booth and Devoy.[8]

Of the suggested explanations, the last seems to us to be the least likely to be correct. Although the molecular weight of WSR-301 is much larger than either 205F or 6100F, the Booth and Devoy benzene activity data are virtually identical for both 205F and 6100F PEO samples, indicating little affect of polymer molecular weight on the results. Such a conclusion is qualitatively corroborated by standard polymer solution theory.

We cannot now determine the cause of the difference between our data and those of Booth and Devoy,[8] but we are at present extending our glc study of benzene in PEO to finite concentration to attempt to resolve the question.

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Polymer Adsorption on a Surface by an Exact Enumeration Study

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ABSTRACTS: The exact enumeration method was used to study the effect the excluded volume constraint has on configurational properties of polymer molecules adsorbed on a planar surface. The adsorbed molecules were computer simulated on a four-choice simple cubic lattice system with the assumption of an energy of adsorption between the polymer atoms and the surface, ranging from 0 to $1.5kT$. The excluded volume constraint is found to have a marked effect on the configurational properties investigated. In particular, the root mean square end-to-end distance data disclose some very interesting observations; namely, that γ shows values greater than 1.2. It appears that the adsorbing surface and energy of adsorption restrict the adsorbed polymer molecule and the system behaves as if it is in a less than three-dimensional environment.

I. Introduction

In the past 20 years much research[2-4] has been accomplished in the theoretical investigation of the mean configurational properties of flexible high-polymer molecules adsorbed on planar surfaces. Only recently has considerable effort been expended to introduce the excluded volume effect[5] into the adsorption treatment. Investigators involved with the simulation of lattice polymers in dilute solutions using the Monte Carlo method[6-9] as well as other investigators using the exact enumeration method[10,11] have shown that the mean-square end-to-end distance, $\langle R_N^2 \rangle$, may be expressed by an equation of the form

$$\langle R_N^2 \rangle = aN^\gamma \tag{1}$$

Domb[12] correlated results for a variety of two- and three-dimensional lattices and concluded that the exponent, γ, should be only a function of dimensionality and independent of any particular lattice structure. He reported the following asymptotic relationships

$$\langle R_N^2 \rangle \cong \begin{cases} A_1(\theta)N^{6/5} + A_2(\theta), & \text{three dimensions} \\ B_1(\theta)N^{3/2} + B_2(\theta)N, & \text{two dimensions} \end{cases} \tag{2}$$

where θ is a parameter related to lattice structure. It turns out that the study of adsorbed polymers offers an opportunity for investigating γ as a function of dimensionality.

II. Model

The exact enumeration method as described by Martin,[13] with modifications to take into account the symmetry of our particular lattice model, was used. The self-avoiding chains ($N \leq 14$ bonds) were simulated on a four-choice simple cubic lattice system with the first atom confined to the origin. The direction of each step of the chain was perpendicular to the direction of the preceding step. The adsorbing surface was taken as the $Z = 0$ plane and no atoms were allowed to go below this plane. Each atom in the $Z = 0$ plane was considered an adsorbed atom and contributed an energy of adsorption ϵ to the Boltzmann factor for the energy of that configuration. If the jth enumerated configuration of the chain of length N has n_{Nj} atoms on the surface, each contributing an energy of ϵ to the total energy of the configuration ($n_{Nj}\epsilon$), then the Boltzmann factor for this configuration is $\exp(-n_{Nj}\epsilon/kT)$. An average parameter of the configurations of the chain of length N, $\langle Z_N \rangle$, is then given by

$$\langle Z_N \rangle = \frac{\sum_{j=1}^{J} Z_{Nj} \exp\left(-\frac{n_{Nj}\epsilon}{kT}\right)}{\sum_{j=1}^{J} \exp\left(-\frac{n_{Nj}\epsilon}{kT}\right)} \tag{3}$$

where Z_{Nj} is the value of the parameter for the jth configuration (for example, squared end-to-end distance) and j is the total number of configurations enumerated.