

Sorption of Solutes by Poly(ethylene Oxide). II. Benzene at Finite Concentrations

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Synopsis

We have determined the activity of benzene in poly(ethylene oxide) over concentration ranges from 0 to 20 wt-% from 70° to 150°C using gas-liquid chromatography. The results are well correlated by the corresponding-states theory of Prigogine and Flory. Comparison between our results and those obtained by other workers using a "static" method indicate good agreement, except at very low benzene concentrations.

INTRODUCTION

We have determined the activity of benzene in poly(ethylene oxide) (PEO) over concentration ranges from 0 to 20 wt-% benzene from 70° to 150°C using gas-liquid chromatography (GLC). The results are correlated using corresponding-states polymer solution theory based on the concepts of Prigogine¹ and Flory.² Good agreement is obtained between the theory and the GLC data.

PEO is a water-soluble polymer which is of commercial importance,³ and the specific chemical interactions which induce water solubility are also of considerable theoretical interest.

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 employing static equilibrium techniques that tend to be slow to reach equilibrium. Since 1969, GLC has been developed and used by several workers (Smidsrød and Guillet,⁴ Guillet and Stein,⁵ Patterson et al.,⁶ Hammers and Deligny,⁷ Newman and Prausnitz,^{8,9,10} Cheng and Bonner,³ and others) to measure the infinite-dilution activity coefficients of a solute vapor over a polymer stationary phase. Concurrently, the application of GLC to polymer thermodynamics in solutions of finite solute concentration was developed in a series of articles by Conder and Purnell.¹¹⁻¹⁵ Conder and Purnell¹⁴ accurately measured the activity coefficients of *n*-hexane in squalane and *n*-heptane in di-*n*-nonyl phthalate over a range of solute concentrations. Brockmeier et al.^{16,17,18} adapted the Purnell and Conder technique of elution on a plateau of finite solute concentration to determine activity coefficients rationalized by

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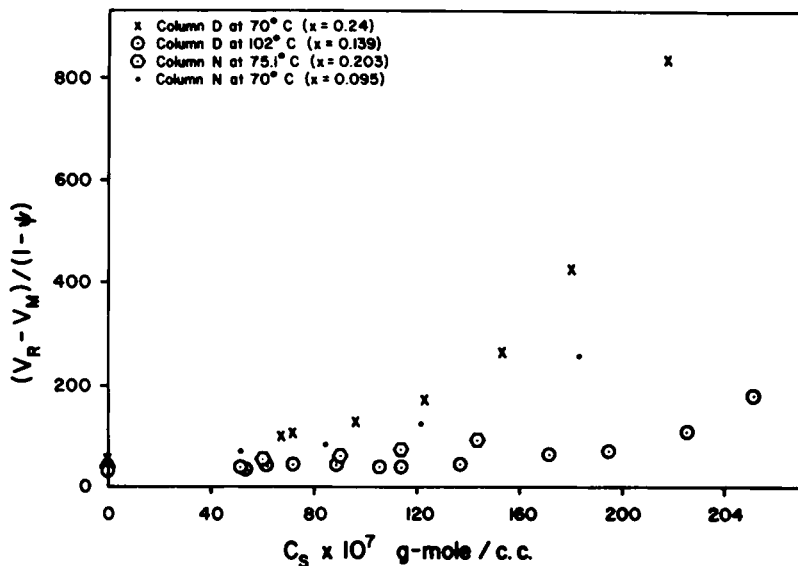


Fig. 1. Plot of $(V_r - V_m)/(1 - \psi)$ vs. solute concentration in carrier gas at 70°C, 75.1°C, and 102°C

weight fraction and polymer-solute interaction parameters for various polymer/solute binary solutions over a range of solute concentrations.

Although increasing attention has been focused on concentrated polymer solutions, there is still a dearth of experimental data concerning solute activity in solutions in which the polymer concentration is greater than 90% by weight. The disadvantage of static equilibrium techniques applied to polymer solutions is that equilibration times in vapor-pressure lowering experiments for concentrated polymer solutions are excessively long: as long as six or seven days.³⁶ However, earlier work cited above has shown that GLC is simple to use, and rapid, and the data are quite reproducible. GLC has many advantages compared to static techniques, especially since GLC has been extended to measure activity coefficients of solute in polymer solution for finite concentrations of solute in solution.

There have been two studies^{20,21,22} concerning water-soluble polymer solutions, and there have been three published articles previous to this work which deal with solute activities in PEO.^{3,20,21,23}

The work described here is significant for two reasons: first, we have investigated sorption of benzene by PEO at several temperatures for which data are not available in the literature; second, we have used the corresponding-states theory of polymer solutions to interpret the experimental data.

EXPERIMENTAL

Apparatus and Procedure

The gas chromatograph used is an F & M 500 equipped with a thermal conductivity detector. The apparatus, which permits the option of using either pure helium as a carrier gas or helium containing a known concentration of solute vapor, is shown schematically in Figure 1 of the previous paper.²⁴

The column oven was rebuilt to provide oven temperature control to $\pm 0.1^\circ\text{C}$ using a Hallikainen Thermotrol and to enable measurement of pressure drop through the column. The temperature in the mineral oil bath is controlled to $\pm 0.05^\circ\text{C}$ by a Sargent thermoregulator. Inlet and outlet column pressures are read to ± 0.1 mm Hg with a mercury monometer. Carrier gas flow rate is measured to 0.2 ml/min (at S.T.P.) using a soap-bubble flowmeter.

A relatively inert carrier gas (usually helium) flows from a high-pressure cylinder through a Negretti and Zambra flow regulator and then into a flask which contains solute. Carrier gas flow rate from the cylinder is controlled by valve (1). Equipment for mixing the helium with solute vapor consists of a 1000-ml round-bottomed flask equipped with a gas diffuser which is connected to a constant-temperature mineral-oil bath. Upon exiting the saturator, the helium contains solute vapor with a partial pressure equal to the saturation vapor pressure of solute at oil-bath temperature. The helium-solute mixture then flows through a tubular column packed with polymer-coated substrate and through a thermal conductivity detector. A small portion of helium-solute mixture controlled by valve (4) goes through a reference line.

The composition of the carrier gas leaving the oil bath is calculated from the vapor pressure of the solute and the total pressure measured by the manometer. A very small amount of the solute (usually 0.1 to 1 μl) together with air is rapidly injected into the flowing carrier gas through a silicone rubber septum with a 1.0- μl or a 10- μl Hamilton gas-tight syringe. The injected solute is then swept by the carrier gas (helium + solute mixture) through the tubular column. Adjusted retention time is obtained by measuring the difference between the retention time of the solute and the retention time of the air. The column inlet and outlet pressure are measured in order to correct column pressure for pressure drop.

A liquid nitrogen condenser is used to condense the solute in the gas mixture, leaving only gaseous helium which flows through the soap-bubble flowmeter. The helium is saturated with water before entering the flowmeter in order to eliminate any uncertainty caused by partial saturation by the soap solution in the bubble flowmeter. Adjusted retention volume is calculated, as shown below, from the adjusted retention time and the helium flow rate.

For infinite-dilution measurements, valve (3) is closed and valve (2) is opened. For finite-concentration measurements, valve (2) is closed and valve (3) is opened to allow helium to enter the flask that contains solute. The solute is maintained at a temperature at or slightly above its boiling point by the heating mantle surrounding the flask. Too great a boiling rate causes liquid solute entrainment into the column and causes the column inlet pressure to fluctuate. The incoming helium passes through the gas diffuser and sweeps the vapor space above the solute but does not bubble through the solute itself. The helium and solute vapor mixture then enters the constant-temperature bath. All connecting tubing is wrapped with heating tape. The heating tape is maintained at a temperature well above the oil bath temperature to ensure that no solute condenses in the tubing. This ensures steady flow rate, and more important, a gas mixture of constant composition between the bath exit and the column inlet. Assuming that the gas imperfection and the solubility of helium in solute are negligible at low operating pres-

sure (~ 0.9 atm), the total pressure measured by the manometer and the oil bath temperature are sufficient to calculate the composition of the solute in the carrier gas. Only manometer (1), which need not be heated, is used during operation. Manometers (2) and (3) are disconnected during operation to prevent solute from condensing in them. The relations among the readings of the three manometers, P_i and P_0 as functions of P_i^1 , must be determined before finite-solute concentration operation. These relations are assumed to hold during finite-solute concentration operation.

Stationary Phase and Solutes

The PEO is Polyox WSR-301 supplied by the Union Carbide Corporation, having a melting range of $65^\circ \pm 2^\circ\text{C}$, specific gravity of 1.21 g/cm^3 at 25°C , and approximate molecular weight of $4 \times 10^6\text{ g/g-mole}$.

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

Solid Supports

Previous work²⁴ has shown that the retention volume of polar and nonpolar solutes in PEO is essentially independent of flow rate, column coverage ratio (weight of polymer/weight of support), and injection amount using Fluoropak 80 (F-80). Columns prepared with F-80 usually give essentially symmetric chromatogram peaks. For this reason, F-80, which is powdered Teflon, has been selected as the support material in this study.

Column Preparation

Columns are prepared by coating the polymer onto F-80. The coating procedure has been discussed by Purnell²⁵ and Littlewood.²⁶ The effect of coating thickness on measured results has been discussed by Aue and Hastings²⁷ and Newman and Prausnitz.^{8,9,10} Previous work²⁴ has shown that PEO may degrade because of thermal oxidation and high shear. The PEO degradation may result in altered column behavior. Therefore, PEO-coated columns must be prepared in a careful way.

The columns are prepared by first dissolving about 0.1 g PEO in chloroform and then stirring the solution with about 10 g F-80. High shear is avoided in the mixing process. The mixture is dried in the air from 5 to 15 hr, being stirred as long as possible. It is then put in a drying oven for several hours. The mixture sample is taken out periodically and weighed until a nearly constant weight is reached. At this time, the chloroform has almost completely evaporated (chloroform odor is absent at this time). Usually, the weight remains constant for about 10 min and is within 0.5% of the original PEO + F-80 weight. At the time nearly constant weight is reached, the amount of PEO decomposed is assumed to be negligible. These columns are the same as those used in previous work.²⁴

DATA REDUCTION

For the technique of solute elution on a plateau of finite concentration, GLC data reduction is accomplished by the method of Conder and Purnell.¹¹⁻

¹⁴ Conder and Purnell have shown that the distribution isotherm at column pressure P is given by

$$q(P) = \frac{j}{m_2} \int_0^{c_1} \frac{V_q - V_r}{1 - \psi} dc_s \quad (1)$$

where $q(P)$ = solute distribution isotherm at column pressure P at temperature T having the dimensions of moles of solute per unit weight of polymer, m_2 = mass of polymer coated on the column, j = a compressibility correction to compensate for the column pressure gradient, ψ = true value of solute vapor mole fraction above the stationary phase at column pressure P and temperature T , V_q = retention volume of solute, V_r = retention volume of air, c_s = solute concentration in the gas above the stationary phase at column pressure P and temperature T , and c_1 = an arbitrary value of c_s . Each term in eq. (1) has been discussed in detail by Conder and Purnell¹¹⁻¹⁴ and by Brockmeier et al.¹⁷

Solute sorption in the PEO causes a residence time difference between solute and air. The relative retention volume is given by

$$V_q - V_r = Q_F(t_q - t_r) \frac{T}{T_F} \quad (2)$$

where t_q = residence time of solute (measured to peak maximum), t_r = residence time of air (measured to peak maximum), Q_F = flow rate measured at T_F , T_F = flowmeter temperature, and T = column temperature.

Helium flow rate Q_F^1 is measured with the soap-bubble flowmeter. Solute is condensed in the liquid nitrogen condenser before the helium stream reaches the flowmeter. Hence, we have

$$Q_F = \frac{Q_F^1}{1 - \psi} \quad (3)$$

where Q_F^1 = helium flow rate measured at T_F with soap-bubble flowmeter. The true value of solute vapor mole fraction above the stationary phase ψ is determined from

$$\psi = a j y_0 \quad (4)$$

where a = gas nonideality correction and y_0 = mole fraction of solute vapor determined from the detector outlet pressure and the oil bath temperature. The gas nonideality correction factor a is defined as

$$a = \frac{b_2^1}{b_3^2} \left[1 + \frac{2y_0 P_0 B_{11}(1 - J_2^1 y_0)}{RT} \right] \quad (5)$$

where P_0 = outlet pressure, R = gas constant, T = system temperature, and B_{11} = second virial coefficient of pure solute at T .

$$J_n^m = \frac{n[(P_i/P_0)^m - 1]}{m[(P_i/P_0)^n - 1]} \quad (6)$$

where P_i = inlet pressure;

$$b_n^m = 1 + k(1 - J_n^m y_0) \quad (7)$$

$$k = (t_q - t_r)/t_r \quad (8)$$

The full compressibility correction factor takes the form

$$j = J_3^2 \left[1 + \frac{y_0^2 P_0 B_{11} (J_3^2 - 1)}{RT} \right] \quad (9)$$

where J_3^2 is a correction for the column pressure gradient. The second term in brackets in eq. (9) compensates for gas-phase nonideality.

The arithmetic mean pressure in a column is defined to be P_2/J_2^1 . The mean pressure in the column for a given isotherm is defined by

$$P = P_0 J_3^4 \quad (10)$$

If the pressure ratio (inlet/outlet) over the column is less than 1.1, this gives values of b_2^1 and b_3^2 which are essentially equal to unity, simplifying some of the calculations.

The solute concentration in the gas above the stationary phase c_s is given by

$$c_s = P_0 \psi / (a_j RT - \psi^2 B_{11} P_0) \quad (11)$$

Conder and Purnell¹³ have suggested that the criterion for constant solute concentration in the gas phase within the column is

$$y_0(P_i - P_0)/P_0 \leq 0.01 \quad (12)$$

Equation (12) must be satisfied to ensure that there is no concentration gradient within the column.

Equation (1), the distribution isotherm, is evaluated from the area under the curve formed by plotting $(V_q - V_r)/(1 - \psi)$ versus c_s , and $c_s = 0$ corresponds to infinite dilution of solute. The weight fraction of solute in the polymer phase is given by

$$w_1 = \frac{q(P)M_1}{1 + q(P)M_1} \quad (13)$$

where M_1 = molecular weight of solute. The partial pressure of solute in the gas above the polymer is

$$P_1 = \psi P = \psi P_0 J_3^4 \quad (14)$$

The activity coefficient of solute rationalized weight fraction is

$$\Omega_1 = \frac{a_1}{w_1} \quad (15)$$

where a_1 = activity of solute. At subatmospheric pressure, the solute activity is

$$a_1 = \frac{P_1}{P_1^0} = \frac{P_0 \psi J_3^4}{P_1^0} \quad (16)$$

where P_1^0 = standard state pressure of pure solute. Equations (15) and (16) are combined to give

$$\Omega_1 = \frac{P_0 \psi J_3^4}{P_1^0 w_1} \quad (17)$$

However, for pressures of 0.5 atm to about 10 atm, eq. (17) is modified to account for gas-phase nonideality:

$$\Omega_1 = \frac{a_1}{w_1} = \frac{P_0 \psi J_3^4}{w_1 P_1^s} \exp\left[\frac{-B_{11}(P_1^s - P_1)}{RT}\right] \quad (18)$$

where P_1^s = saturated pressure of solute. The standard state in eq. (18) is pure, saturated liquid solute at system temperature.

EFFECT OF PEO DEGRADATION

Earlier work²⁴ has shown that PEO degrades easily. Degradation is significant during the experiments when system temperature is high. The PEO degradation has two main effects on the GLC results: (a) the characteristics of PEO/solute solution may be changed if the degradation is sufficiently great; (b) the degradation should be taken into account in the data reduction to obtain the true PEO weight. The PEO degradation is tentatively ascribed to depolymerization.

Based on the discussion of earlier work,²⁴ eq. (1) is modified to give

$$q(P) = \frac{j}{m_2^0(1-x)} \int_0^{c_1} \frac{V_q - V_r}{1-\psi} dc_s \quad (19)$$

where x = fractional weight loss of polymer in the column and m_2^0 = original weight of polymer. If $x \neq 0$, then taking x into account gives

$$q(P) = \frac{j}{m_2^0(1-x)} \int_0^{c_1} \frac{V_q - V_r}{1-\psi} dc_s = \text{true value.} \quad (20)$$

Not taking x into account gives

$$q'(P) = \frac{j}{m_2^0} \int_0^{c_1} \frac{V_q - V_r}{1-\psi} dc_s = \text{apparent value.} \quad (21)$$

Dividing eq. (21) by (20) gives

$$1 - x = \frac{q'(P)}{q(P)} \quad (22)$$

or

$$x = \frac{q(P) - q'(P)}{q(P)} \quad (23)$$

where the true value of $q(P)$ is equal to that of the first reference $q(P)$ determined when x is zero, assuming constant temperature.

The integral term in eq. (19) complicates calculation of $q(P)$ and hence calculation of x . An alternate way of determining x is to make infinite-dilution measurements. From previous study,²⁴ we have

$$x = \frac{V_g^0 - V_g^{0'}}{V_g^0} \quad (24)$$

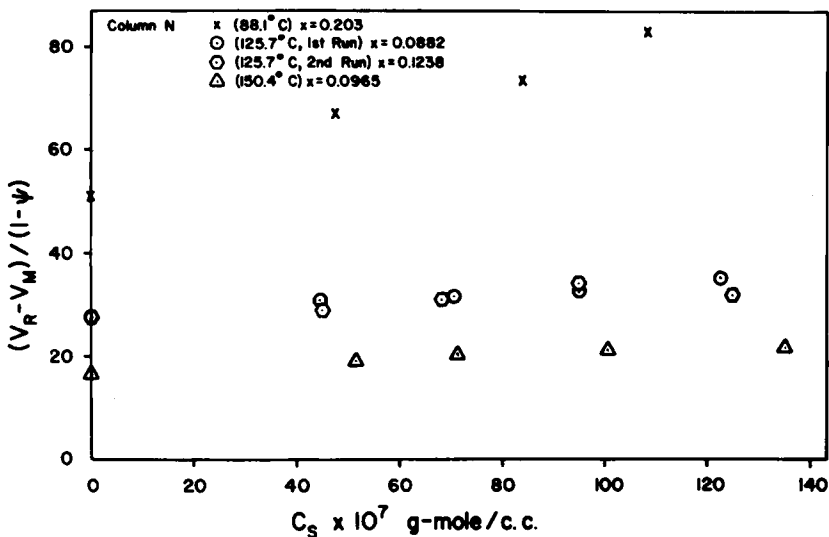


Fig. 2. Plot of $(V_r - V_m)/(1 - \psi)$ vs. solute concentration in carrier gas at 88.1°C, 125°C, and 150.4°C.

where $V_g^0 = Q(t_q - t_r) (273.2/T) f_p/m_2^0(1 - x)$ = true value, $V_g^{0'} = Q(t_q - t_r) (273.2/T) f_p/m_2^0$ = apparent value, 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), f_p = pressure drop correction factor so that V_g^0 is corrected to average column pressure = $3/2[(P_i/P_0)^2 - 1]/[(P_i/P_0)^3 - 1]$. The true value of V_g^0 is equal to that of the first reference value of V_g^0 determined when x is zero, assuming constant temperature.

Since the work described here was completed within five months, the columns used for infinite-dilution and finite-concentration studies are the same. The PEO degradation history for each column has been shown previously.²⁴

Because there is no reliable means of determining changes in x in the finite-concentration studies, we have assumed x to be constant during a given finite-concentration run. Fortunately, each isotherm can be obtained within one day, and x is nearly constant during that period. If, during determination of an isotherm, the change in x was significant, that isotherm was rejected.

Column D ($0.139 \leq x \leq 0.24$) was used to obtain two isotherms at 70° and 102°C. Column N ($0.096 \leq x \leq 0.120$) was used to obtain isotherms from 70° to 150°C.

RESULTS

Figures 1 and 2 show the experimental GLC data obtained from columns D and N for the benzene/PEO system at temperatures from 70 to 150.4°C. The results are plotted so that the area under the curve is equal to the integral in eq. (19). The product of the area and $j/[m_2^0(1 - x)]$ gives the solubility $q(p)$ at each concentration c_s of solute in the carrier gas.

Tables I-IV show the weight fraction of solute (w_1) determined from eq.

TABLE I
Weight Fraction (w_1) and Activity Coefficient Ω
of Benzene in Solutions of Poly(ethylene Oxide) WSR-301

70.0°C First run		70°C Second run	
w_1	Ω_1	w_1	Ω_1
0.06163	4.3118	0.05005	4.1031
0.06711	4.2311	0.08908	3.7426
0.0991	3.8095	0.1422	3.3435
0.1387	3.4739	0.2006	2.9955
0.1926	3.0925	0.2649	2.7017
0.261	2.6898		
0.3881	2.1527		
$\Omega_1^\infty = 4.572$		$\Omega_1^\infty = 4.572$	
Conditions:		Conditions:	
1. Column D after 24% PEO wt loss		1. Column N after 9.5% PEO wt loss	
2. Flow rate: 19.3 ml/min (S.T.P.)		2. Flow rate: 24.7 ml/min (S.T.P.)	
3. Injection amount: 0.5 μ l		3. Injection amount: 0.5 μ l	

(13) and the activity coefficients of solute rationalized by weight fraction (Ω_1) at each w_1 for temperatures from 70° to 150°C determined from eq. (18). Based on the work of Patterson et al.,⁶ the infinite-dilution activity coefficient Ω_1^∞ is determined from

$$\Omega_1^\infty = \left(\frac{a_1}{w_1}\right)^\infty = \frac{273.16R}{V_g^0 P_1^s M_1} \exp\left[\frac{-P_1^s B_{11}}{RT}\right] \quad (25)$$

B_{11} is calculated based on the work of Pitzer and Curl.³⁸ P_1^s is calculated from the Antoine equation:^{28,29}

$$\log_{10} P = A - B/(t + C) \quad (26)$$

with $A = 6.90565$ for 100–160°C, $B = 1211.033$ for 100–160°C, $C = 220.79$, P [=] mm Hg, t [=] °C, and

$$\log_{10} P = -\frac{0.05223a}{T} + b \quad (27)$$

TABLE II
Weight Fraction (w_1) and Activity Coefficient Ω
of Benzene in Solutions of Poly(ethylene Oxide) WSR-301

75.1°C First run		88.1°C Second run	
w_1	Ω_1	w_1	Ω_1
0.05254	3.9837	0.02687	4.2337
0.08096	3.7549	0.05012	3.9859
0.1083	3.5608	0.06671	3.8503
0.1454	3.3316	0.0906	3.6668
$\Omega_1^\infty = 4.5625$		$\Omega_1^\infty = 4.608$	
Conditions:		Conditions:	
1. Column N after 20.3% PEO wt loss		1. Column N after 20.3% PEO wt loss	
2. Flow rate: 12 ml/min (S.T.P.)		2. Flow rate: 18 ml/min (S.T.P.)	
3. Injection amount: 0.5 μ l		3. Injection amount: 0.5 μ l	

TABLE III
Weight Fraction (w_1) and Activity Coefficient Ω
of Benzene in Solutions of Poly(ethylene Oxide) WSR-301

102°C First run		150.4°C Second run	
w_1	Ω_1	w_1	Ω_1
0.02076	4.3033	0.007975	4.3113
0.02192	4.2801	0.01130	4.2015
0.02502	4.2717	0.01635	4.0606
0.02919	4.2248	0.02256	3.9560
0.03687	4.1477		
0.04418	4.0704		
0.04777	4.0423		
0.05834	3.9496		
0.07706	3.7134		
0.09184	3.5198		
0.1180	3.1694		
$\Omega_1^\infty = 4.572$		$\Omega_1^\infty = 4.6084$	
Conditions:		Conditions:	
1. Column D after 13.9% PEO wt loss		1. Column D after 9.65% PEO wt loss	
2. Flow rate: 18.6 ml/min (S.T.P.)		2. Flow rate: 10.9 ml/min (S.T.P.)	
3. Injection amount: 0.5 μ l		3. Injection amount: 0.5 μ l	

with $a = 03395$ for 42–100°C, $b = 7.6546$ for 42–100°C, $a = 34172$ for 0–42°C, $b = 7.9622$ for 0–42°C, $P [=]$ mm Hg, and $t [=]$ °K. In the calculation, eq. (27) is used for 70° to 100°C; eq. (26) is used for 102° to 150°C.

COMPARISON WITH OTHER WORKERS

Booth and Devoy²⁰ have reported activity coefficients of benzene in PEO at 70°C. The comparison of our GLC results and the static results of Booth and Devoy is shown in Figure 3. The agreement is fair. The discrepancies at very low solute concentration are ascribed to the inaccuracy of determining x , since from eq. (19) x has significant effect on the results when c_1 is very small. That is, $(V_q - V_r)$ is affected by x ($V_q - V_r = 0$, if $x = 1$), and $\int_0^{c_1} (V_q - V_r)/(1 - 4)dc_s$ is small if c_1 is small; the inaccuracy in calculating the smaller integral area may result in a higher per cent error in the results.

TABLE IV
Weight Fraction (w_1) and Activity Coefficient Ω
of Benzene in Solutions of Poly(ethylene Oxide) WSR-301

125.4°C First run		125.7°C Second run	
w_1	Ω_1	w_1	Ω_1
0.01094	4.249	0.01115	4.1547
0.01769	4.1411	0.01734	4.0733
0.02392	4.0804	0.02474	3.9452
0.03278	3.9928	0.03313	3.8742
$\Omega_1^\infty = 4.4997$		$\Omega_1^\infty = 4.4997$	
Conditions:		Conditions:	
1. Column N after 8.82% PEO wt loss		1. Column N after 12.38% PEO wt loss	
2. Flow rate: 15.5 ml/min (S.T.P.)		2. Flow rate: 10.3 ml/min (S.T.P.)	
3. Injection amount: 0.5 μ l		3. Injection amount: 0.5 μ l	

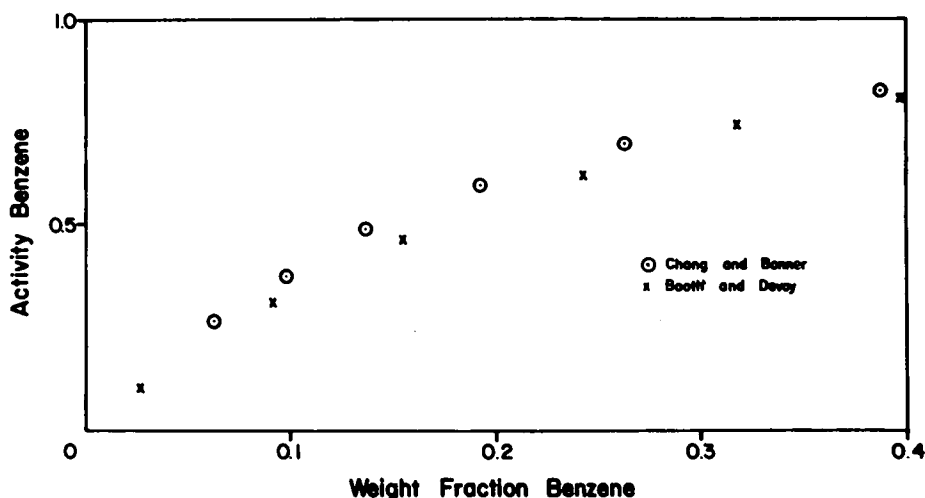


Fig. 3. Comparison of static data with GLC data at 70°C.

THEORETICAL CORRELATION OF RESULTS WITH CORRESPONDING-STATES THEORY OF POLYMER SOLUTIONS

Booth and Devoy²⁰ have compared their static results of sorption of benzene in PEO with the Flory-Huggins theory. Deviations from theory are ascribed to specific charge-transfer interactions in the mixture.

Prigogine et al.^{1,30,31} developed a corresponding-states theory for polymer solutions which attempts to account for noncombinatorial contributions in a more rigorous and realistic way than does the Flory-Huggins theory. Several workers have used the Prigogine concept of a corresponding-states theory for polymer solutions: Simha and Hadden,³² Hijmans and Holleman,³³ Patterson,³⁴ Flory,³⁵ Bonner and Prausnitz,¹⁹ Bonner et al.,³⁷ and others. Bonner and Prausnitz¹⁹ and Bonner et al.³⁷ have discussed application of the corresponding-states theory in detail. Their formulas are summarized as follows: The activity of solute a_1 is given by

$$a_1 = \Psi_1 \exp \left\{ (1 - r_1/r_2) \Psi_2 + \frac{P_1^* M_1 v_{1sp}^*}{RT_1^*} \times \right. \\ \left. \left[3 \ln \left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right) + 1/\tilde{T}_1 (1/\tilde{v}_1 - 1/\tilde{v}) \right] + \right. \\ \left. \frac{\Psi_2^2 M_1 v_{1sp}^*}{RT\tilde{v}} (P_1^* + P_2^* - 2P_{12}^*) \right\} \quad (28)$$

with the standard state being pure, saturated solute at system temperature T . Solute segment fraction Ψ_1 is given by

$$\Psi_1 = w_1 v_{1sp}^* / (w_1 v_{1sp}^* + w_2 v_{2sp}^*) = 1 - \Psi_2 \quad (29)$$

where $w_1 = 1 - w_2 =$ weight fraction of solute in the solution v_{1sp}^* , P_1^* , and T_1^* are characteristic parameters of the solute, and v_{2sp}^* , P_2^* , and T_2^* are characteristic parameters of the polymer. M_1 is the solute molecular weight,

R is the gas constant, and T is absolute temperature, \bar{v} is reduced molar volume of the solution, and \bar{v}_1 is reduced molar volume of the solute.

The characteristic specific volume v_{sp}^* is the hard-core volume of one gram of fluid. The characteristic temperature T^* is a measure of the potential energy per external degree of freedom. The characteristic pressure P^* is a characteristic potential energy density. The characteristic parameters are related by

$$P^* \left(\frac{M v_{sp}^*}{r N_A} \right) = ckT^* \quad (29')$$

where N_A = Avogadro constant, k = Boltzmann constant, M = molecular weight, r = number of segments, and $3c$ = number of external degrees of freedom per segment. Bonner and Prausnitz¹⁹ report the following characteristic parameters for benzene and PEO:

$$\begin{aligned} v_{1sp}^* &= 0.890 \text{ ml/g} \\ P_1^* &= 5770 \text{ atm} \} \text{ for } 0\text{-}200^\circ\text{C} \\ T_1^* &= 4780^\circ\text{K} \\ v_{2sp}^* &= 0.753 \text{ ml/g} \\ P_2^* &= 6720 \text{ atm} \} \text{ for } 45\text{-}70^\circ\text{C} \\ T_2^* &= 6450^\circ\text{K} \end{aligned}$$

We used the above values for all calculations. The segment ratio r_1/r_2 is given by

$$\frac{r_1}{r_2} = \frac{M_1 v_{1sp}^*}{M_2 v_{2sp}^*} \quad (30)$$

as suggested by Flory.² The reduced volume of pure solute \bar{v}_1 is equal to v_{1sp}/v_{1sp}^* , where v_{1sp} is the solute specific volume. The quantity \bar{v}_1 is obtained by solving the equation of state for pure solute at zero pressure formally the same as eq. (31). The mixture reduced volume \bar{v} is obtained from the equation of state of the mixture at zero pressure:

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}} \quad (31)$$

where

$$T^* = P^* / (\Psi_1 P_1^* / T_1^* + \Psi_2 P_2^* / T_2^*) \quad (32)$$

$$P^* = \Psi_1^2 P_1^* + \Psi_2^2 P_2^* + 2\Psi_1 \Psi_2 P_{12}^* \quad (33)$$

The characteristic pressure P_{12}^* is given by

$$P_{12}^* = (P_1^* P_2^*)^{1/2} (1 - \Delta) \quad (34)$$

where Δ is a measure of the deviation of the only binary interaction parameter P_{12}^* from the geometric mean of P_1^* and P_2^* . P_{12}^* , and hence Δ , can be obtained by fitting binary solution data.

We have used the corresponding-states theory described above to correlate our GLC results and the results of Booth and Devoy at atmospheric pressure and temperatures from 70° to 150°C. The data and optimal theoretical cor-

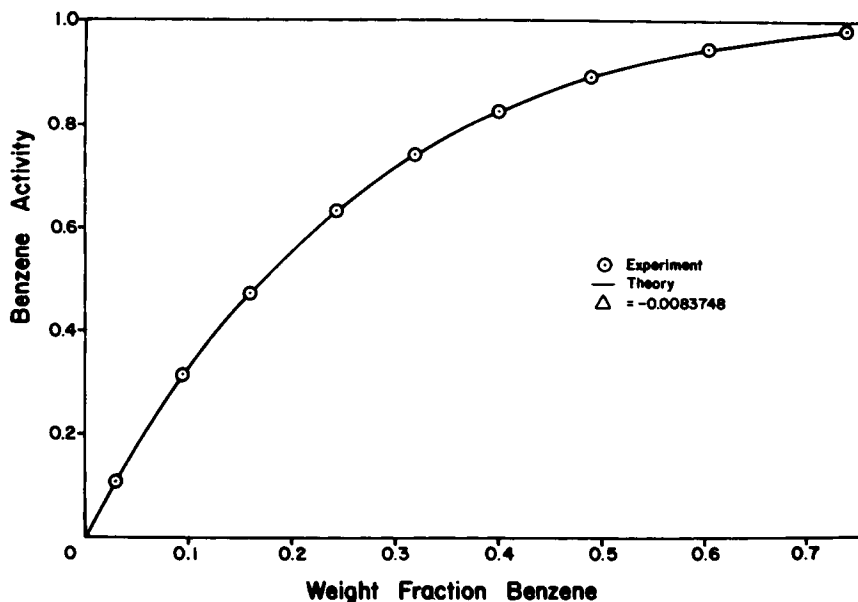


Fig. 4. Correlation of experimental data of Booth and Devoy^{20,21} at 70°C with corresponding-states polymer solution theory.

relations are shown in Figures 4 to 8. The solid lines in Figures 4 to 8 are the optimal correlations of the data using eq. (28). The optimal correlations were obtained by a nonlinear regression analysis to determine values of Δ by minimizing the sum of the squares of per cent errors of solute activity for each data set. The experimental data are all correlated very well by the theory, as shown in Figures 4 to 8.

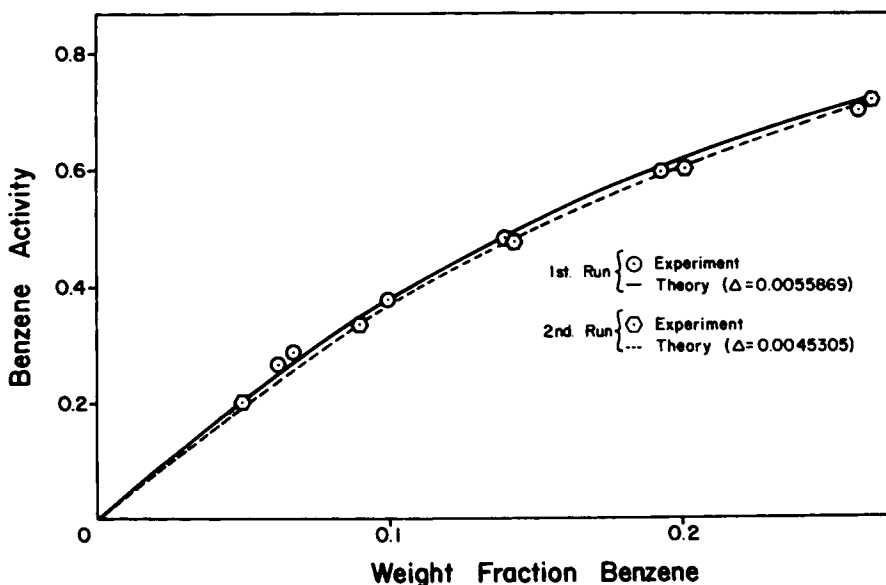


Fig. 5. Correlation of GLC experimental results at 70°C with corresponding-states polymer solution theory.

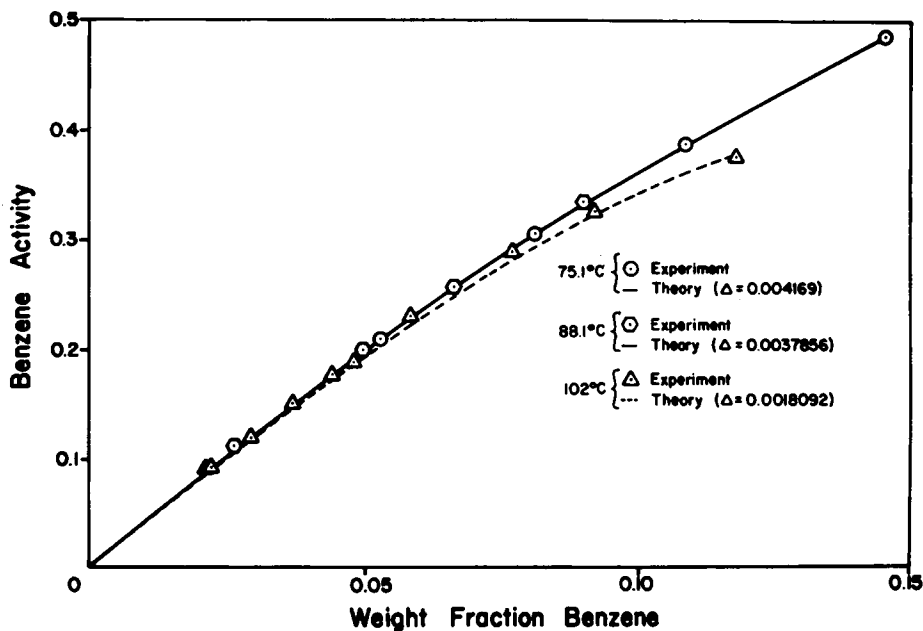


Fig. 6. Correlation of GLC experimental results at 75.1°C, 88.1°C, and 120°C with corresponding-states polymer solution theory.

The binary interaction parameter P_{12}^* (and Δ) obtained from regression correlation of data are shown in Table V. It is worthwhile to note that Δ has a very small value, which means that the geometric mean approximation for P_{12}^* is reasonably accurate. Furthermore, the temperature dependence of Δ (or P_{12}^*) is very weak. The activity coefficient of benzene in PEO is shown

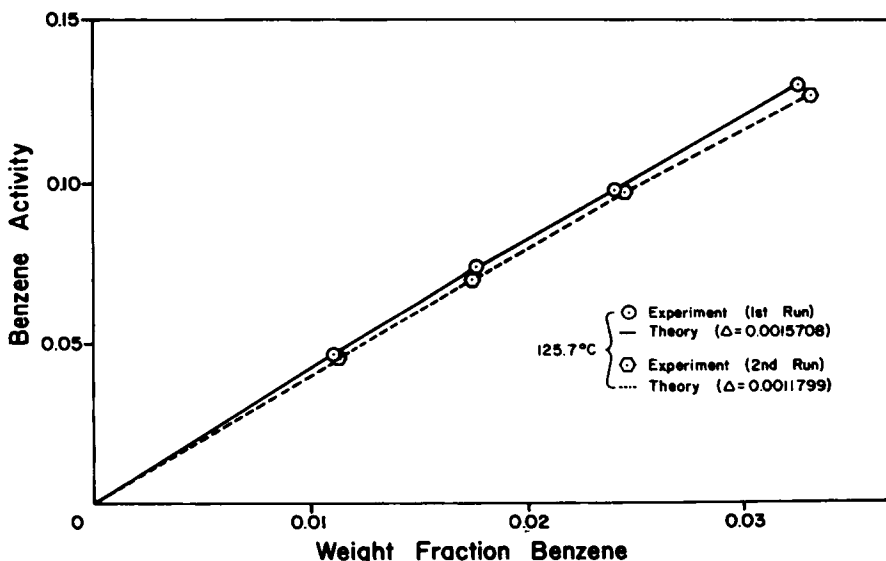


Fig. 7. Correlation of GLC experimental results at 125.7°C with corresponding-states polymer solution theory.

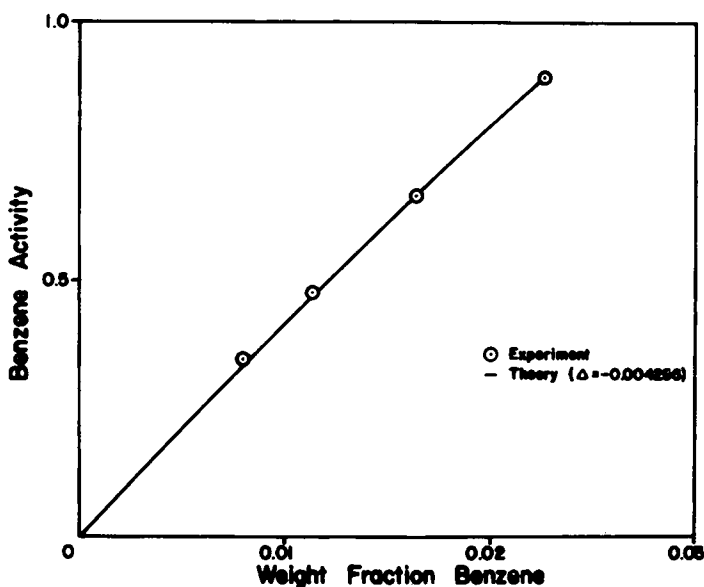


Fig. 8. Correlation of GLC experimental results at 150.4°C with corresponding-states polymer solution theory.

in Table VI. The activity coefficient of benzene in PEO is essentially independent of temperature. The reasons for this are not clear, but the temperature independence may be due in part to cancellation of volumetric changes by intermolecular force and electron donor-acceptor interactions.

CONCLUSIONS

We have used GLC to obtain activity coefficients of benzene in PEO over the concentration range 0 to 10 wt-% of benzene from 70° to 150°C. PEO

TABLE V
Binary Interaction Parameters for Benzene/PEO Solution

Data obtained	Temperature, °C	Δ	P_{12}^* , atm
GLC Column N	70	0.0055869	6192.12
GLC Column D	70	0.0045305	6198.70
Booth and Devoy	70	-0.0083748	6232.12
GLC Column N	75	0.004169	6200.95
GLC Column N	88	0.0037856	6203.34
GLC Column D	102	0.0018092	6215.64
GLC Column N (1st)	125	0.0015708	6217.13
GLC Column N (2nd)	125	0.0011799	6226.18
GLC Column N	150	-0.0042559	6229.56

TABLE VI
Infinite Activity Coefficient of Benzene in PEO^a

Temperature	70°C	75.1°C	88.1°C	102°C	125.7°C	150.4°C
Ω_1^∞	4.572	4.563	4.608	4.572	4.50	4.6084

^a Obtained from previous study.²⁴

degradation effects have been taken into account as accurately as possible. Each isotherm can be obtained within one day. We have used the corresponding-states theory of polymer solutions to correlate our GLC results. The theory correlates the data very well. The behavior of PEO/benzene solution at different temperatures is discussed. Comparison of our GLC results and the static results of other workers shows fair agreement.

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