

Sorption of solutes by poly(ethylene oxide): 3. Partial molar entropy and enthalpy in poly(ethylene oxide) solution with benzene

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The partial molar entropy and enthalpy of benzene in poly(ethylene oxide) solution have been determined over concentration ranges from 0 to 20 wt % for temperatures from 70° to 150°C using the corresponding-states theory of Prigogine and Flory. These results show that both the partial molar entropy and enthalpy of benzene in poly(ethylene oxide) increase as the segment fraction of poly(ethylene oxide) increases and decrease as temperature increases. The partial molar enthalpy is positive from 70° to 150°C.

INTRODUCTION

The purpose of this paper is to obtain the partial molar entropy and the partial molar enthalpy of benzene in poly(ethylene oxide) (PEO) from 70° to 150°C. From these results, certain conclusions concerning the nature of the benzene/PEO solution can be reached.

The activity (a_1) of a low molecular weight solvent (subscript 1) dissolved in a polymer (subscript 2) may be resolved into its entropy and enthalpy components in either of two ways: the partial molar enthalpy may be measured directly by calorimetric methods and the partial molar entropy calculated from the relationship:

$$\bar{s}_1 = (\bar{h}_1 - R T \ln a_1) / T \quad (1)$$

where \bar{s}_1 is the partial molar entropy, \bar{h}_1 is the partial molar enthalpy, and a_1 is the activity of solvent; or the temperature coefficient of the activity may be determined, and from it the partial molar entropy and enthalpy may be calculated using the following relationships:

$$\bar{h}_1 = -RT^2 \left(\frac{\partial \ln a_1}{\partial T} \right)_{p, \psi_2} \quad (2)$$

$$\bar{s}_1 = -R \left[T \left(\frac{\partial \ln a_1}{\partial T} \right)_{p, \psi_2} + \ln a_1 \right] \quad (3)$$

where p and ψ_2 are pressure and segment fraction of polymer (to be defined later), respectively.

The calorimetric method has been applied successfully only to polymers of relatively low molecular weight where the viscosity of the concentration solution is not great. The high viscosity of most concentrated polymer solutions presents serious problems in measurement of the small heats of mixing or dilution. The second method requires very great precision in measurement of activity in order that the usually small temperature coefficient can be determined with sufficient accuracy.

Chiang and Bonner^{1,2} determined the activity of benzene in PEO over concentration ranges from 0 to 20 wt % for

temperatures from 70° to 150°C using gas-liquid chromatography and obtained good agreement in comparing their results with those obtained by other workers using a 'static' method. In this paper, we use the results of Chiang and Bonner² to obtain the partial molar enthalpy and the partial molar entropy of benzene in PEO.

THEORY

Prigogine *et al.*³ developed a corresponding-states theory for polymer solutions which attempts to account for non-combinatorial contributions to chemical potential in a more rigorous and realistic way than does the Flory-Huggins⁴ theory. Bonner and Prausnitz⁵ and Bonner⁶ have discussed application of the corresponding-states theory in detail. Their equations are summarized below for solvent (1)/polymer (2) solutions. The activity of solvent is given by⁵:

$$a_1 = \psi_1 \exp \left\{ (1 - r_1/r_2) \psi_2 + \frac{p_1^* M_1 v_{1sp}^*}{RT_1^*} \times \left[3 \ln \left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right) + \frac{1}{\tilde{T}_1} \left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right) \right] + \frac{\psi_2^2 M_1 v_{1sp}^*}{RT_1^* \tilde{v}} (p_1^* + p_2^* - 2p_{12}^*) \right\} \quad (4)$$

with the standard state being a pure, saturated solvent at system temperature T . Solvent segment fraction (ψ_1) is given by:

$$\psi_1 = w_1 v_{1sp}^* / (w_1 v_{1sp}^* + w_2 v_{2sp}^*) = 1 - \psi_2 \quad (5)$$

where $w_1 = 1 - w_2 =$ weight fraction of solvent in the solution, the segment ratio r_1/r_2 is given by:

$$\frac{r_1}{r_2} = \frac{M_1 v_{1sp}^*}{M_2 v_{2sp}^*} \quad (6)$$

Table 1 Characteristic parameters for benzene and PEO

Component	v_{sp}^* (m ³ /kg)	p^* (Pa)	T^* (K)
Benzene	0.890×10^{-3}	5.847×10^8	4.78×10^3
PEO	0.753×10^{-3}	6.809×10^8	6.45×10^3

Table 2 Binary interaction energy density (p_{12}^*) for benzene/PEO solution at different temperatures (T)

T (K)	1/T (K ⁻¹)	p_{12}^* (Pa)	$\ln p_{12}^*$ (Pa)
First run, 343.2	2.914×10^{-3}	6.2745×10^8	20.2572
Second run, 343.2	2.914×10^{-3}	6.2811×10^8	20.2582
First run, 348.2	2.872×10^{-3}	6.2834×10^8	20.2586
Second run, 361.2	2.769×10^{-3}	6.2858×10^8	20.2590
First run, 375.2	2.665×10^{-3}	6.2983×10^8	20.2610
Second run, 423.2	2.363×10^{-3}	6.3124×10^8	20.2632
First run, 398.2	2.511×10^{-3}	6.2998×10^8	20.2612
Second run, 398.2	2.511×10^{-3}	6.3090×10^8	20.2627

as suggested by Flory⁷, M_1 is the solvent molecular weight, R is the gas constant, and T is the absolute temperature, v_1^* , p_1^* , T_1^* and v_2^* , p_2^* , T_2^* are characteristic parameters of solvent (1) and polymer (2), respectively. Bonner and Prausnitz⁵ reported characteristic parameters for benzene and PEO, and these are given in Table 1.

The terms $\tilde{v}_1 = v_{1sp}/v_{1sp}^*$ and $\tilde{v} = v_{sp}/v_{sp}^*$ are reduced volume of pure solvent and of solution, respectively, and are obtained by solving the equation of state for pure solvent and for the mixture at zero pressure:

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}} \quad (7)$$

The equation of state is formally the same for pure components and for mixtures. The reduced temperature \tilde{T} is given by:

$$\tilde{T} = \frac{T}{T^*} \quad (8)$$

$$T^* = p^*/(\psi_1 p_1^*/T_1^* + \psi_2 p_2^*/T_2^*) \quad (9)$$

$$\text{Also, } p^* = \psi_1^2 p_1^* + \psi_2^2 p_2^* + 2\psi_1 \psi_2 p_{12}^* \quad (10)$$

$$p_{12}^* = (p_1^* p_2^*)^{1/2} (1 - \Delta) \quad (11)$$

where Δ is a measure of the deviation of the binary interaction parameter p_{12}^* from the geometric mean of p_1^* and p_2^* . Values of p_{12}^* , and hence Δ , can be obtained by fitting binary solution data.

The characteristic specific volume v_{sp}^* , temperature T^* and pressure p^* are measures of the hard-core volume of one gram of fluid, the potential energy per external degree of freedom, and the potential energy density, respectively. The characteristic parameters are related by:

$$p^* \left(\frac{M v_{sp}^*}{r N_A} \right) = c k T^* \quad (12)$$

where N_A is Avogadro's number; k is Boltzmann's constant; M is the molecular weight; r is the number of segments per

molecule; $3c$ is the number of external degrees of freedom per segment. In differentiating the corresponding-states equation, we face the problem of determining the temperature dependence of p_{12}^* . Bonner and Prausnitz⁵ reported the values of the binary interaction parameter p_{12}^* for twenty binary polymer/solvent solutions at different temperatures. Their data show that the binary interaction energy density is a function of temperature. Chiang and Bonner² obtained values of the binary interaction energy density of benzene in PEO from 70° to 150°C. Their results are shown in Table 2. From these data, the logarithm of p_{12}^* is found to be proportional to the inverse of the absolute temperature:

$$\ln p_{12}^* = a + b/T \quad (13)$$

Using the method of least squares, we obtain:

$$a = 20.2873 \text{ and } b = -10.1171$$

The relationship of $\ln p_{12}^*$ and $1/T$ is shown in Figure 1. The standard deviation in p_{12}^* given by equation (13) is equivalent to $\pm 0.06\%$ average absolute deviation.

To obtain the partial molar enthalpy of benzene in PEO, we use equation (2). The differentiation of the corresponding-states equation is shown as follows:

$$\left(\frac{\partial \ln a_1}{\partial T} \right)_{p, \psi_2} = \left(\frac{k_1}{\tilde{T}_1} - \frac{k_1}{\tilde{T}} - \frac{k_2 k_3}{T} \right) \left(\frac{1/T^*}{\frac{4}{3} \tilde{v}^{-1/3} - 1} \right) \times$$

$$\left(1 + \frac{b k_6 p_{12}^*}{T^* T k_4} \right) + \frac{k_1}{\tilde{T}_1 T} \left(\frac{1}{\tilde{v}} - \frac{1}{\tilde{v}_1} \right) +$$

$$k_2 \left(\frac{2 b p_{12}^*}{\tilde{v} T^3} - \frac{k_3}{\tilde{v} T^2} \right) \quad (14)$$

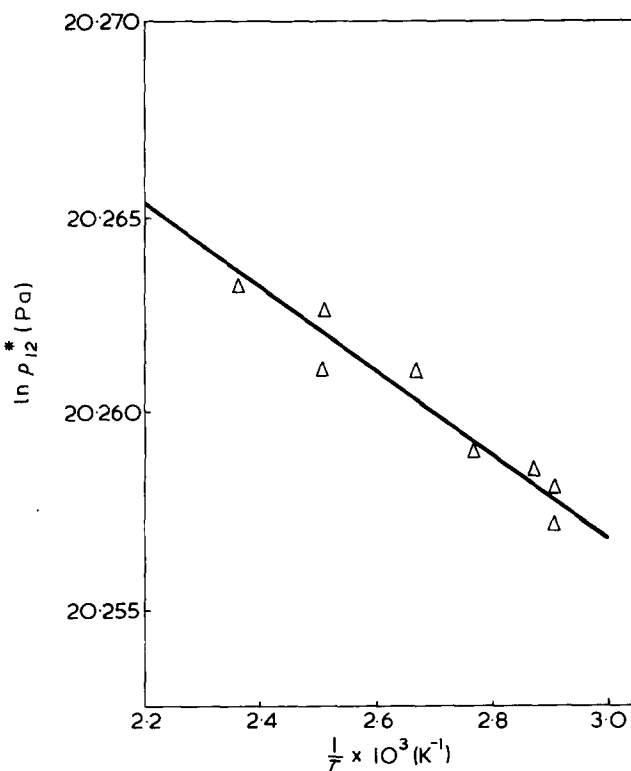


Figure 1 Variation of p_{12}^* with temperature

Table 3 Partial molar entropy (\bar{s}_1) and enthalpy (\bar{h}_1) in benzene/PEO solution

T(K)	w ₁	ψ ₂	\bar{s}_1 (J/mol K)	\bar{h}_1 (J/mol)
First run 343.2	0.06163	0.9280	19.39	2681
	0.06711	0.9216	18.68	2646
	0.0991	0.8849	15.42	2451
	0.1387	0.8401	12.61	2222
	0.1926	0.7801	9.91	1935
	0.2610	0.7055	7.47	1606
	0.3881	0.5715	4.47	1092
Second run 343.2	0.05005	0.9414	21.09	2671
	0.08908	0.8964	16.26	2435
	0.1422	0.8362	12.37	2138
	0.2006	0.7713	9.54	1837
	0.2649	0.7013	7.32	1542
First run 348.2	0.05254	0.9385	20.43	2586
	0.08096	0.9057	16.82	2417
	0.1083	0.8745	14.40	2259
	0.1454	0.8326	11.97	2061
Second run 361.2	0.02687	0.9685	25.34	2579
	0.05012	0.9413	20.08	2440
	0.06671	0.9221	17.78	2343
	0.0906	0.8947	15.26	2209
First run 375.2	0.02076	0.9756	26.57	2259
	0.02502	0.9706	25.02	2234
	0.03687	0.9567	21.80	2171
	0.04418	0.9482	20.33	2130
	0.04777	0.9440	19.67	2112
	0.05834	0.9317	18.03	2056
	0.07706	0.9102	15.73	1958
	0.09184	0.8932	14.31	1884
	0.1180	0.8435	12.29	1757
Second run 423.2	0.00798	0.9906	30.77	1004
	0.01130	0.9867	27.88	987
	0.01635	0.9807	24.84	966
	0.02256	0.9734	22.18	940
First run 398.2	0.01094	0.9871	30.28	1845
	0.01769	0.9792	26.30	1810
	0.02392	0.9719	23.81	1777
	0.03278	0.9615	21.22	1732
Second run 398.2	0.01115	0.9869	30.02	1709
	0.01734	0.9796	26.37	1678
	0.02474	0.9709	23.44	1642
	0.03313	0.9611	21.03	1602

$$\text{where } k_1 = \frac{p_1^* M_1 v_{1,sp}^*}{RT_1^*}$$

$$k_2 = \psi_2^2 \left(\frac{M_1 v_{1,sp}^*}{R} \right)$$

$$k_3 = p_1^* + p_2^* - 2p_{12}^*$$

$$k_4 = \frac{p_1^* \psi_1}{T_1^*} + \frac{p_2^* \psi_2}{T_2^*}$$

$$k_5 = p_1^* \psi_1^2 + p_2^* \psi_2^2$$

$$k_6 = 2\psi_1 \psi_2$$

The term b is the slope of equation (13); in benzene/PEO solution, $b = -10.1171\text{K}$.

Flory and Huggins⁴ developed a lattice theory which

represents, among other things, the activity of solvent, partial molar entropy, and partial molar enthalpy:

$$\bar{h}_1^* = RT\chi\psi_2^2 \quad (15)$$

$$\bar{s}_1^* = -R \ln(1 - \psi_2) + (1 - r_1/r_2)\psi_2 \quad (16)$$

$$a_1 = \psi_1 \exp[(1 - r_1/r_2)\psi_2 + \chi\psi_2^2] \quad (17)$$

where \bar{h}_1^* is partial molar enthalpy of solvent due to Flory–Huggins theory, \bar{s}_1^* is partial molar entropy of the solvent due to Flory–Huggins theory, r_1/r_2 is the ratio of the number of segments per solvent molecule to that for polymer, and χ is a dimensionless, empirical quantity characterizing the interaction energy per solvent molecule. From equation (16), we find that the partial molar entropy, \bar{s}_1^* , is expressed as a function of the segment fraction of solute and is not explicitly a function of temperature.

RESULTS AND DISCUSSION

Substituting values of characteristic parameters for benzene and PEO into equation (14) and making use of equation (2), values of the partial molar entropy and enthalpy of benzene in PEO are obtained. Table 3 shows the values of partial molar entropy and the enthalpy for benzene concentrations from 0 to 20 wt % for the temperature range 70° to 150°C. The average variation of \bar{h}_1 , is $\pm 1.2\%$ at 343.2K and $\pm 3.3\%$ at 423.6K. Similar values for \bar{s}_1 are $\pm 0.12\%$ and $\pm 0.45\%$ at 243 and 423.6K, respectively.

The partial molar entropy (\bar{s}_1^*) from Flory–Huggins polymer solution theory is expressed as a function of the segment fraction of solute and is not an explicit function of temperature. The partial molar entropy (\bar{s}_1) from the corresponding-states theory is a function of the segment fraction of solute as well as a function of temperature. We obtain the partial molar entropy (\bar{s}_1) and the enthalpy (\bar{h}_1) from the corresponding-states theory and compare them with the partial molar entropy (\bar{s}_1^*) and the enthalpy (\bar{h}_1^*) from Flory–Huggins theory to show how these thermodynamic functions are influenced by temperature.

The partial molar entropy (\bar{s}_1) from the corresponding-states theory and that (\bar{s}_1^*) from Flory–Huggins theory for the temperature range from 70° to 150°C are plotted versus the segment fraction (ψ_2) of PEO in benzene in Figures 2–4. The partial molar enthalpy (\bar{h}_1) from the corresponding-states theory and that (\bar{h}_1^*) from Flory–Huggins theory are shown in Figures 5–7. All these Figures indicate that the four thermodynamic functions (\bar{s}_1 , \bar{s}_1^* , \bar{h}_1 and \bar{h}_1^*) increase as the segment fraction of solute (ψ_2) increases and decrease as temperature increases.

Booth and Devoy⁸ showed that there exists some charge transfer between benzene and PEO. It is therefore unexpected that both \bar{h}_1 and \bar{h}_1^* from our data from benzene/PEO solution are positive.

The partial molar entropy and the enthalpy data for benzene/PEO solution obtained by Booth and Devoy⁸ are shown in Table 4. Booth and Devoy⁸ conclude, as we do, that both the partial molar entropy and enthalpy increase as the segment fraction of solute increases, and decrease as temperature increases. However, the values of the partial molar entropy and enthalpy they obtained are lower than our partial molar entropy and enthalpy values. Their partial molar enthalpy is negative, while ours is positive.

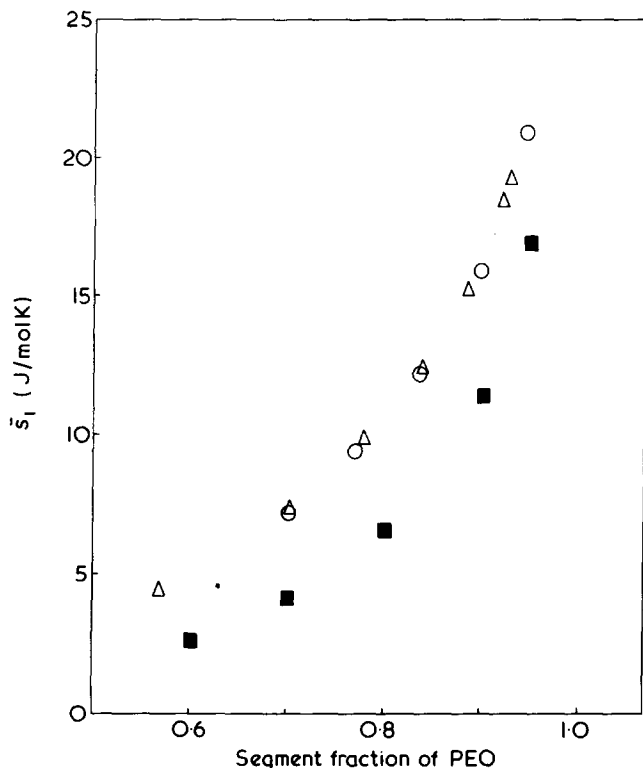


Figure 2 Partial molar entropy of benzene in PEO solution at 343.2K: Δ , first run; \circ , second run; \blacksquare , Flory-Huggins theory

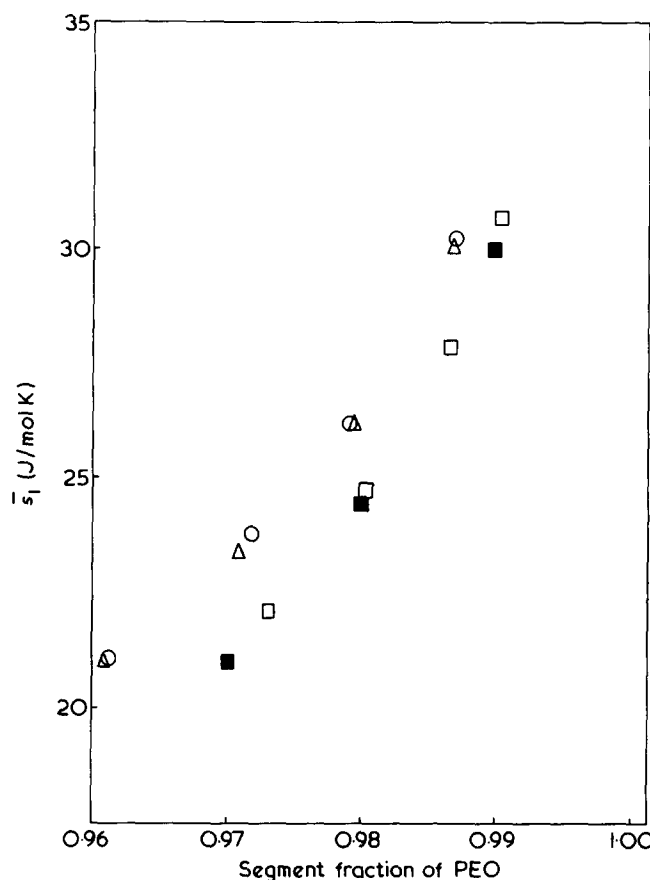


Figure 4 Partial molar entropy of benzene in PEO solution: \circ , 398.2K first run; Δ , 398.2K second run; \square , 423.2K second run; \blacksquare , Flory-Huggins theory

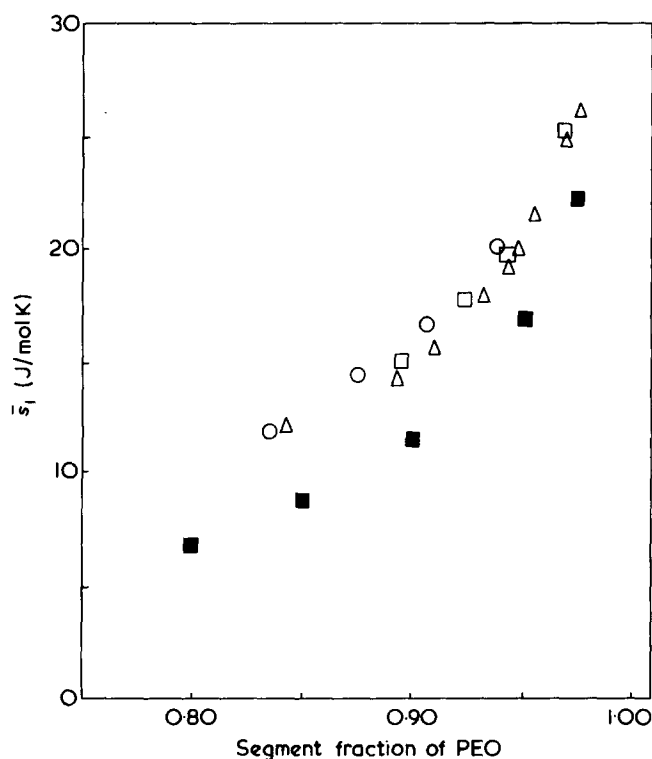


Figure 3 Partial molar entropy of benzene in PEO solution \circ , 348.2K; \square , 361.2K; Δ , 375.2K; \blacksquare , Flory-Huggins theory

There are several possible reasons for the sign difference in \bar{h}_1 obtained by the authors and by Booth and Devoy⁸. First, the molecular weight of the polymer we used was substantially greater than those of the samples used by Booth and Devoy (4×10^6 g/gmol versus 5700 g/gmol and 6×10^5 g/mol). The high molecular weight sample of Chiang and

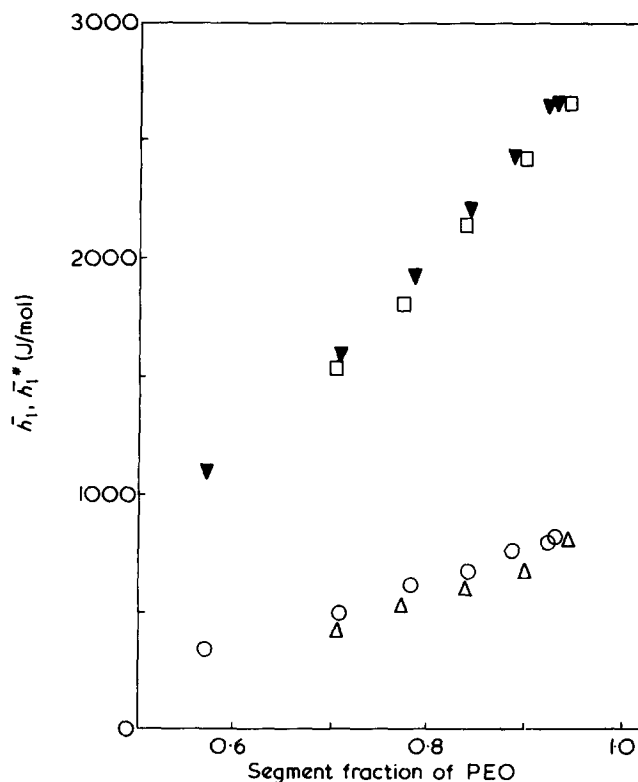


Figure 5 Partial molar enthalpy of benzene in PEO solution at 343.2K: \blacktriangledown , \bar{h}_1 first run; \circ , \bar{h}_1^* first run; \square , \bar{h}_1 second run; Δ , \bar{h}_1^* second run

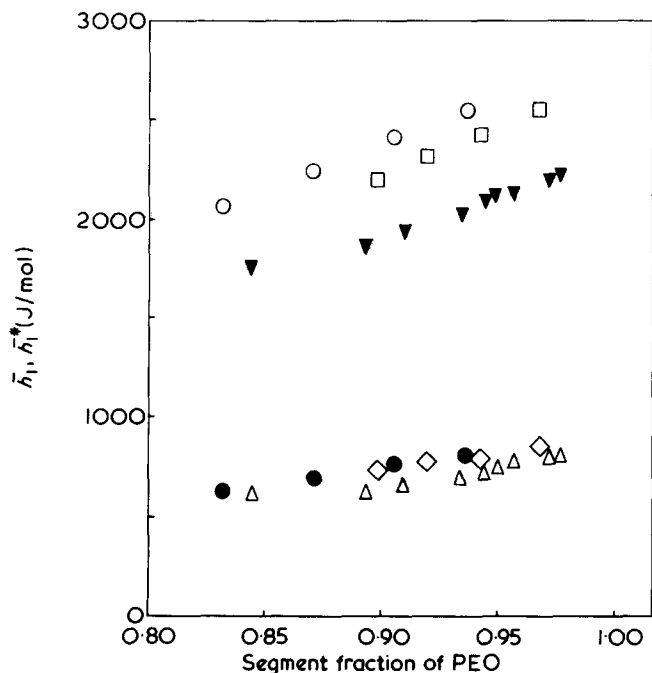


Figure 6 Partial molar enthalpy of benzene in PEO solution: \circ , \bar{h}_1 at 348.2K; \bullet , \bar{h}_1^* at 348.2K; \square , \bar{h}_1 at 361.2K; \diamond , \bar{h}_1^* at 361.2K; \blacktriangledown , \bar{h}_1 at 375.2K; \triangle , \bar{h}_1^* at 375.2K

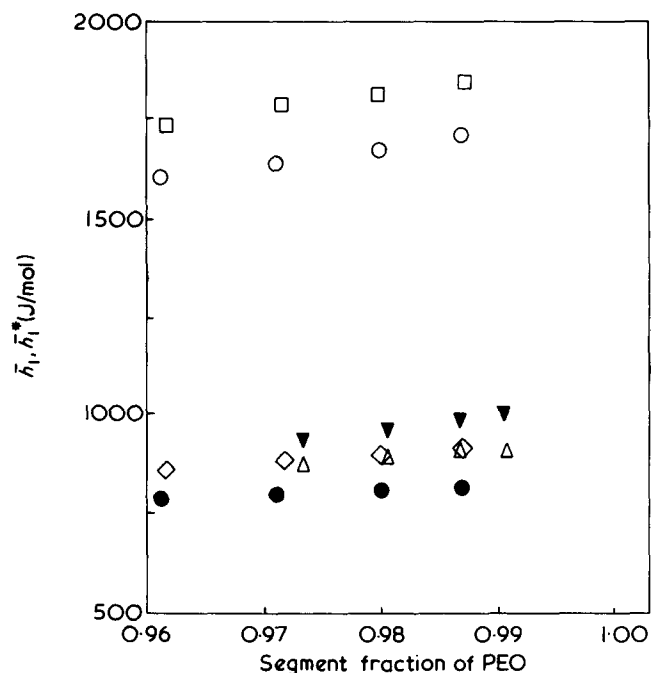


Figure 7 Partial molar enthalpy of benzene in PEO solution: \square , \bar{h}_1 at 398.2K, first run; \diamond , \bar{h}_1^* at 398.2K, first run; \bullet , \bar{h}_1 at 398.2K, second run; \blacktriangledown , \bar{h}_1^* at 398.2K second run; \blacktriangledown , \bar{h}_1 at 423.2K; \triangle , \bar{h}_1^* at 423.2K

Bonner^{1,2} could have a higher melting range than the Booth and Devoy⁸ samples. If the melting range of the Chiang and Bonner sample extends to 70°C, the \bar{h}_1 and \bar{s}_1 values could be influenced by fusion phenomena.

Second, determination of \bar{h}_1 was done differently. Booth and Devoy⁸ determined \bar{h}_1 graphically at the mean of two temperatures, which can lead to considerable uncertainty in the results.

The third and perhaps most significant difference between

Table 4 Partial molar entropy and enthalpy for benzene/PEO solution from Booth and Devoy⁸

PEO sample	ψ_2	\bar{s}_1 (J/mol K)	\bar{h}_1 (J/mol)
6000F at 331.1K	0.664	1.36	-481
	0.559	0.59	-346
	0.458	0.22	-232
	0.361	0.05	-142
205F at 333.3K	0.664	1.19	-544
	0.559	0.44	-393
	0.458	0.11	-266
	0.361	-0.03	-169

the results presented here and those of Booth and Devoy⁸ is that the temperature range in which our data were taken is above the melting range of PEO (~66°C). The data taken by Booth and Devoy⁸ are at temperatures at or below the melting range of PEO, except possibly for their sample of 5700 molecular weight. Although the presence of benzene solvent minimizes the effect of melting transition, hydrogen bonding and other contributors to order become more significant at lower temperatures, possibly reversing the sign of \bar{h}_1 .

Baba *et al.*⁹ have reported heat of dilution values for oligomeric ethylene oxide/benzene solutions at 25°C. The number-average molecular weight of the largest oligomer considered by Baba *et al.*⁹ was 1000 g/gmol. For that oligomer, the change of the heat of dilution per mole of benzene was reported to be positive and of a similar order of magnitude to \bar{h}_1 values reported by us. This indicates that charge transfer is probably not the dominant effect determining \bar{h}_1 . In addition, the behaviour of \bar{h}_1 determined from our data is normal in the sense that it approaches the Flory-Huggins value as temperature increases.

Turning now to \bar{s}_1 results, one sees in Figures 2 and 4 that from 70° to 150°C, \bar{s}_1 values are substantially greater than the \bar{s}_1^* values predicted by Flory-Huggins theory. This may indicate that the addition of benzene to the solution has a much more disruptive effect on solution order than assumed by the Flory-Huggins development.

A final comment should be made regarding the discrepancy between the signs of \bar{h}_1 reported by Booth and Devoy⁸ and by us. The sign of \bar{h}_1 may change as a function of molecular weight¹⁰ and as a function of temperature. Work is in progress in our laboratory to determine systematically the effects of molecular weight and temperature on \bar{h}_1 values for benzene/PEO solutions.

CONCLUSIONS

The corresponding-states theory of polymer solutions has been used to obtain values of \bar{h}_1 and \bar{s}_1 for benzene/PEO solutions from 70° to 150°C. The values of \bar{h}_1 obtained are positive, agreeing with the results of Baba *et al.*⁹ but disagreeing with those of Booth and Devoy⁸. Our results indicate that charge transfer is probably not the dominant effect governing \bar{h}_1 from 70° to 150°C. The values of \bar{s}_1 indicate that the solution is significantly more disrupted by the addition of benzene than is assumed by the Flory-Huggins model.

Work is in progress in our laboratory to determine in a more systematic way the effects of polymer molecular weight and temperature on \bar{h}_1 in benzene/PEO solutions.

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