

Sorption of benzene by poly(ethylene oxide)

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The activity of benzene in poly(ethylene oxide), PEO, has been determined over the concentration range 0.3 to ~35 wt % benzene using the piezoelectric sorption method. The temperature range was 64° to 97°C and the molecular weights of polymer samples were 1.0×10^5 , 6.0×10^5 , and 5.0×10^6 g/g mol. The Flory–Huggins interaction parameters, χ , determined in this work agree within experimental error with χ values determined by gas chromatography and by vapour pressure measurement. The values of χ extrapolated to zero solvent concentration, χ^∞ , have a minimum and negative value in the vicinity of 85°C for the sample of molecular weight 1.0×10^5 , 84°C for the sample of molecular weight 6.0×10^5 , and 77°C for the sample of molecular weight 5.0×10^6 . In the vicinity of 65°C, χ^∞ is negative for each molecular weight of polymer and increases to positive values with an increase in temperature. For all samples studied, the χ^∞ parameters reach constant values (0.22 to 0.30) at temperatures higher than 90°C.

INTRODUCTION

Investigations of thermodynamic properties of concentrated polymer solutions have been made by gas chromatography^{1–6}, vapour pressure measurement^{7,8}, heat of mixing measurement^{9–12}, vapour sorption measurement^{13–22} and high pressure osmometry^{16–22}. According to the original Flory–Huggins theory of polymer solution thermodynamics²³, which assumes that the polymer–solvent interaction parameter χ is independent of solution composition, the solvent activity coefficient ($\Gamma_1 = a_1/\psi_1$) in the neighbourhood of zero solvent concentration (ψ_1) decreases with an increase in ψ_1 by an exponential function such as $\exp(\psi_2 + \chi\psi_2^2)$ for infinite molecular weight polymer. It has been recognized from experiment^{9–12,15–22} that the χ parameter for some concentrated polymer solutions decreases with an increase of solvent concentration. This behaviour of χ corresponds to a more rapid decrease function for Γ_1 with an increase of ψ_1 as compared to that predicted by original Flory–Huggins theory.

The recent theories of polymer solution thermodynamics by Flory^{24,25} and Patterson^{26,27} successfully predict the composition dependence of χ and the corresponding activity coefficient decrease by taking into account the free volume effect or 'equation of state' contribution and by introducing the 'site fraction' in polymer solutions. It is also possible to take into account, at least semiquantitatively, adsorption of solvent by polymer in addition to the contribution from the difference in free volumes and intermolecular forces in concentrated polymer solutions²⁸.

On the other hand, examinations of the basic assumptions in the original and recent Flory theories and the Patterson theory have been made experimentally and theoretically. The importance of inhomogeneity in concentrated polymer solution, which is not explicitly taken into account by the Flory theory, was first stressed by Zimm²⁹ through the calculation of a clustering function, derived by Kirkwood and Buff³⁰, by using solvent activity in polymer solutions³¹.

An approximation for non-randomness in polymer solutions as an alternative to the random mixing approximation

of most polymer solution models has been proposed by Prausnitz *et al.*³² by introducing the concept of local composition.

In a recent theory of polymer solutions due to Huggins³³, orientational entropy arising from concentration dependence of orientation is taken into account in addition to 'combinatorial entropy'. The importance of orientational order in polymer solution thermodynamics has also been pointed out by Patterson^{9–12,15} through the examination of the quantitative differences of the χ parameter in theory and experiment. However, the morphology and configurations of polymer chains in the amorphous state^{34,35} should be important in discussing the solvent activity coefficient in polymer solutions in the vicinity of zero solvent concentration²⁸.

In this work, we have determined the activity coefficient of benzene in a semicrystalline polymer, poly(ethylene oxide), PEO, by using the piezoelectric sorption method in the concentration range of 0.3 to 35 wt% benzene over a temperature range of 64° to 97°C. The molecular weights of the polymer were $M = 1.0 \times 10^5$, 6×10^5 , and 5×10^6 g/g mol. We also discuss the characteristics of benzene vapour sorption by PEO in the vicinity of zero solvent concentration using the Kirkwood–Buff and Zimm theories of solution thermodynamics and morphological data.

EXPERIMENTAL

The PEO samples used in this work were obtained from Scientific Polymer Products, Inc. The molecular weights of PEO samples were 1.0×10^5 , 6.0×10^5 , and 5.0×10^6 g/g mol. The benzene solvent (certified 99 mol % pure) was obtained from Fisher Scientific Company.

The apparatus used to measure the sorption of benzene in PEO was designed for operation from vacuum to 4 atm pressure and is a modification of that used by Bonner and Cheng¹³ for pressures to 140 atm. The apparatus in this work consists of five parts.

Part one is the source of solvent, a solvent-filled flask, which is heated at approximately constant temperature by a controlled mantle heater.

Part two, described previously³, is a water bath controlled to $\pm 0.1^\circ\text{C}$, in which coiled stainless steel tubing about 3 m long and 4 mm i.d. is connected to the solvent source. The tubing connecting the bath coil and solvent source is heated to temperatures greater than the flask and bath temperatures. The temperature of the flask was always set slightly greater than that of the water bath in order for the benzene vapour in the coiled tubing in the water bath to reach saturation with liquid benzene. The constant, equilibrium vapour pressure in the coiled tubing is supplied to the system when the sorption of vapour by polymer is measured. Therefore, the pressure in the system is equal to the saturated vapour pressure of the solvent at the temperature of the bath.

Part three is a cell machined out of a stainless steel test cross block (75 × 50 × 50 mm) with a quartz crystal mounted inside¹³. The temperature of the oven, in which the test block is housed, is controlled to $\pm 0.1^\circ\text{C}$ and set at a temperature higher than that of the water bath. The crystal (diameter, 10 mm; electrode diameter, 5 mm; thickness, ~ 0.5 mm) is a type SP 7 AT-Cut, with a 10 MHz base frequency and 10 pF capacitance, supplied by Sentry Manufacturing Co. The two electrodes of the crystal were soldered to two silver alloy (1.6% silver) rods which are insulated by glass-filled nylon sheaths and penetrate the cell. Teflon tape is used in the screw threads of the cell to help eliminate leakage. Each silver alloy rod was connected to the crystal oscillator circuit (Part four).

Part four is a variable frequency crystal oscillator circuit with an SN7404N integrated circuit. The power supply is a 5 V d.c., 50 mA controlled voltage source. The frequency of the crystal was monitored by a Hewlett-Packard 5302 A Universal Frequency Counter connected to a Hewlett-Packard 5300 A digital display, which displays frequency to 1 Hz (sampling 1 sec) and 0.1 Hz (10 sec).

Part five is a vacuum system to evacuate the sorption system and to minimize changes in the measured frequency caused by the sorption of water or air. The vacuum pump we use is a GCA/Precision Scientific model DD-20 with an ultimate vacuum of 0.5×10^{-2} torr (1 torr = 1 mmHg).

Coating solutions were prepared by dissolving PEO in benzene at 30° to 40°C to make a solution of about 0.02 to 0.1 wt %. Solutions of 0.10 wt % PEO in benzene, with $M = 5.0 \times 10^6$ and 6.0×10^5 , show fibrous or viscoelastic properties at about 30°C . In this case a more dilute coating solution is used to minimize any effect on crystal vibration due to viscoelastic behaviour of the polymer. One drop of filtered solution was placed on each side of the crystal, and the solution was allowed to spread over the crystal surface uniformly.

Before coating the polymer on the crystal, the temperature of cell and crystal were kept constant at each measuring temperature for 3 to 4 h. All benzene from the coating solutions had evaporated under vacuum at operating temperature after 2 to 4 h, and constant crystal frequency was achieved.

According to the mass sensitivity of 2600 Hz per μg reported by King³⁶, the amount of PEO coated on the crystal in this work was about 0.3 to 1.5 μg of polymer (about 100 to 700 Å thick assuming that the entire surface of the crystal is coated uniformly with liquid polymer), corresponding to frequency change of 800 to 4000 Hz. The amount of benzene absorbed was about 0.04 to 0.4 μg (about 10 to 200 Å thick assuming the entire surface of the crystal is coated uniformly with liquid benzene), corresponding to the frequency change of 100 to 1000 Hz. Each measurement at a different

cell temperature and different molecular weight of polymer was started by measuring the frequency of the pure crystal.

After each isotherm was obtained, the PEO coated on the crystal was removed by washing with water 2 or 3 times and then with ethanol at room temperature and dried under vacuum until the original frequency of pure crystal was regained.

DATA REDUCTION

Sauerbrey³⁷ derived a relation between frequency decrease and the mass of material deposited on the crystal surface:

$$\Delta F = 0.38 \times 10^6 \frac{F \Delta m}{t A} \quad (1)$$

where ΔF is the frequency decrease of the vibrating crystal due to the applied mass Δm (g), F is the frequency of the vibrating crystal (MHz), t is the thickness of the crystal plate (cm), and A is the area of electrode coating (cm^2). In this work the weight fraction of benzene absorbed by PEO was calculated using equation (1):

$$w_1 = \Delta m' / (\Delta m' + \Delta m_0) = \Delta F' / (\Delta F' + \Delta F_0) \quad (2)$$

where $\Delta F'$ is the frequency decrease due to the benzene mass ($\Delta m'$) absorbed by PEO on the crystal, and ΔF_0 is the frequency decrease due to the initially applied polymer coating of mass Δm_0 .

At equilibrium between the benzene vapour phase and the PEO-benzene solution phase, the fugacity of benzene in the vapour phase equals the fugacity of benzene in the liquid phase. At modest pressure, the activity coefficient of solvent a_1 at solution temperature (TK) is expressed by²⁸:

$$a_1 = \frac{p_1}{p_1^s} \exp \left[\frac{-B_{11}(p_1^s - p_1)}{RT} \right] \quad (3)$$

where p_1 is the partial pressure of benzene above PEO-benzene solution, p_1^s is the saturation vapour pressure of benzene at solution temperature, B_{11} is the second virial coefficient of benzene, and R is the gas constant. The standard state used for equation (3) is pure, saturated benzene at solution temperature. In this work, p_1 and p_1^s are the saturation vapour pressure of benzene at the temperature of water bath and at that of cell, respectively.

The values of p_1 and p_1^s for pure benzene³⁸ are calculated from

$$\log_{10} p = A - B/(t + C) \quad (4)$$

where $A = 6.89772$, $B = 1203.531$, $C = 219.888$, p (mmHg) and t ($^\circ\text{C}$). The second virial coefficient (B_{11}) of benzene³⁹ is given by

$$B_{11} = 70 - 1320 \times 10^5 / T^2 \text{ cm}^3/\text{g mol} \quad (5)$$

RESULTS

The weight fraction activity coefficient of solvent, $\Omega_1 (= a_1/w_1)$, has been determined using equations (2) and (3). The values of weight fraction for various coating thicknesses

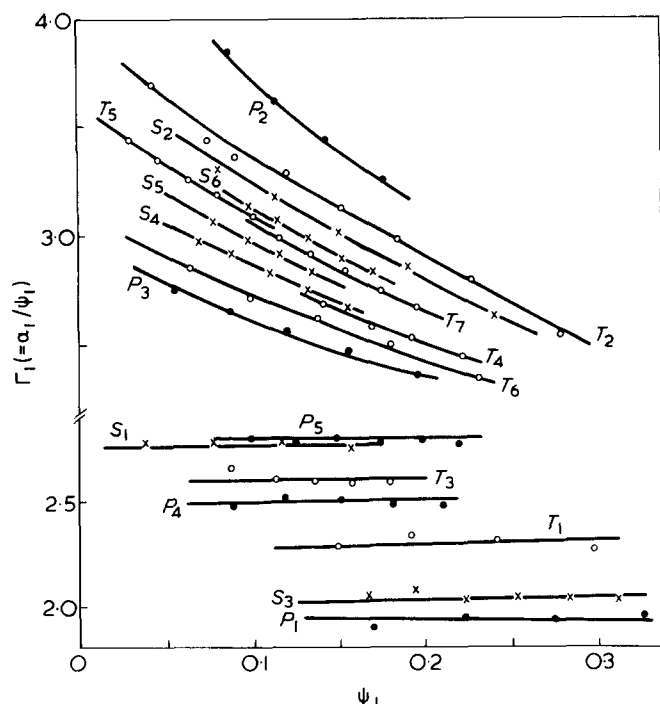


Figure 1 Segment fraction activity coefficient ($\Gamma_1 = a_1/\psi_1$) vs. segment fraction solvent (ψ_1) in the poly(ethylene oxide) ($M = 1.0 \times 10^5$, (T); 6.0×10^5 , (S); 5.0×10^6 , (P)) / benzene system at various temperatures: $T_1 = 64.5^\circ\text{C}$, $T_2 = 74.7$, $T_3 = 85.0$, $T_4 = 87.7$, $T_5 = 89.5$, $T_6 = 90.6$, $T_7 = 95.3$; $S_1 = 65.5$, $S_2 = 70.7$, $S_3 = 85.7$, $S_4 = 89.4$, $S_5 = 91.9$, $S_6 = 95.1$; $P_1 = 65.9$, $P_2 = 73.3$, $P_3 = 75.7$, $P_4 = 76.9$, $P_5 = 79.8$

of PEO on the crystal agreed within an absolute error of 1 to 3%. The errors were due to frequency fluctuations (± 5 Hz). The error caused by temperature fluctuation ($\pm 0.1^\circ\text{C}$) in determining activity a_1 was about 0.5%. The effect of thermal degradation of PEO³ has been taken into account by monitoring the decrease of the amount of PEO on the crystal, or the increase of frequency of the coated crystal under vacuum.

It is normally the practice to analyse polymer-solvent interactions using the Flory-Huggins formulation for activity coefficient (Γ_1):

$$\Gamma_1 = a_1/\psi_1 = \exp[(1 - 1/r)\psi_2 + \chi\psi_2^2] \quad (6)$$

where the ψ 's represent volume fractions of solvent (1) and polymer (2) and r is the ratio of molar volume of polymer to that of solvent. Following more recent polymer solution theory, we take the ψ values to be segment fractions²⁵:

$$\psi_i = x_i v_i^* / (x_1 v_1^* + x_2 v_2^*) \quad (7)$$

where x is mole fraction and v is hard-core volume. Another, more practical recipe for segment fraction is

$$\psi_i = w_i v_{i,sp}^* / (w_1 v_{1,sp}^* + w_2 v_{2,sp}^*) \quad (8)$$

where $v_{i,sp}^*$ is the specific characteristic volume reduction parameter of component (i). In the PEO-benzene system, the values of specific characteristic volumes are $v_{1,sp}^* \approx 0.890 \text{ cm}^3/\text{g}$ for benzene³ and $v_{2,sp}^* = 0.753 \text{ cm}^3/\text{g}$ for PEO³.

Typical values of the segment fraction activity coefficient Γ_1 for the solution of PEO ($M = 1.0 \times 10^5$, 6.0×10^5 , and 5.0×10^6) in benzene are plotted against segment fraction of benzene (ψ_1) in Figure 1.

In Figure 2, typical values of χ are plotted against ψ_1 for the solution of benzene in PEO ($M = 6.0 \times 10^5$). The temperature dependence of the χ parameter extrapolated to zero solvent concentration (χ^∞) is shown in Figures 3 and 4. The precision of the values of χ is approximately $\pm 2\%$. The values of χ^∞ are precise to approximately $\pm 3\%$. The precision of another quantity we will discuss later, $(\partial\chi/\partial\psi)^\infty$, is approximately $\pm 4\%$.

DISCUSSION

The activity of benzene (a_1) against weight fraction of benzene (w_1) in PEO obtained in this work is compared with a_1 determined from gas chromatography by Chang and Bonner³ and from vapour pressure measurement by Booth and Devoy⁷ in Figure 5. The numerical difference of a_1 between our method and gas chromatography or vapour pressure measurement should largely be ascribed to error in determining the weight fraction of solvent. For example, in this work the absolute error of w_1^2 due to frequency fluctuation (± 5 Hz) is approximately 2 to 4%, depending on the coating amount of polymer. However, good agreement between our method and gas chromatography and vapour pressure measurements is obtained within experimental error. The χ^∞ values determined by gas chromatography and vapour pressure measurements are also compared with those of our method in Figures 3 and 4. The agreement between our method and gas chromatography is noteworthy because of the difference in procedure. For example, the polymer used in the measurement of gas chromatography is first crystalline and then molten above the melting point of PEO, while in our method the polymer samples (order of μg) are coated from dilute polymer solution with less than 0.10 wt % of polymer on a heated crystal at constant measuring temperature.

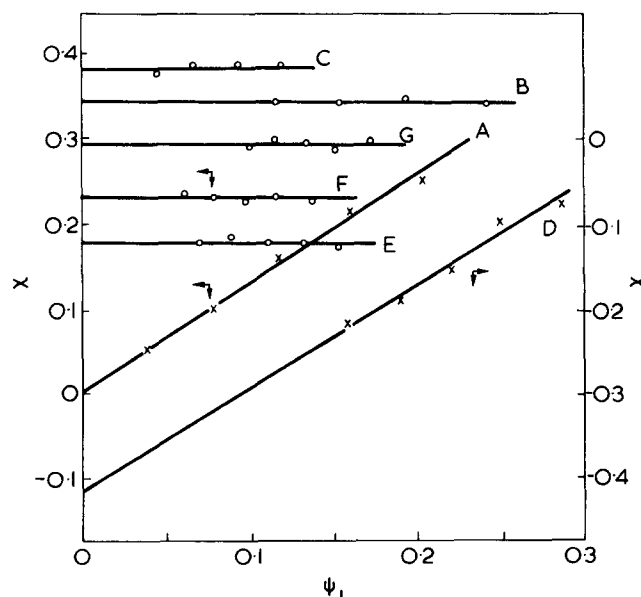


Figure 2 Interaction parameter (χ) vs. segment fraction of solvent (ψ_1) in the poly(ethylene oxide) ($M = 6.0 \times 10^5 \text{ g/g mol}$) / benzene system at various temperatures: A, 65.5°C ; B, 70.7 ; C, 75.3 ; D, 82.2 ; E, 89.4 ; F, 91.9 ; G, 95.1

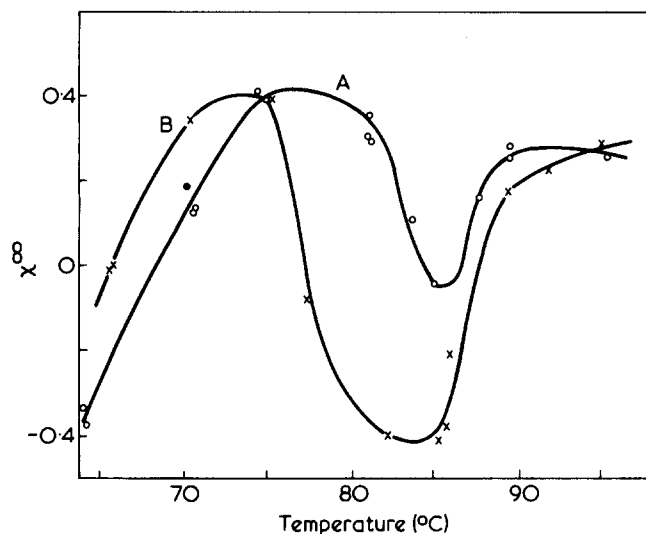


Figure 3 Interaction parameter extrapolated to zero solvent concentration, χ^∞ , vs. temperature in the poly(ethylene oxide) ($M = 1.0 \times 10^5$, A; $M = 6.0 \times 10^5$, B)/benzene system. ●, are values from vapour pressure measurement of Booth and Devoy⁷ ($M = 6.0 \times 10^5$)

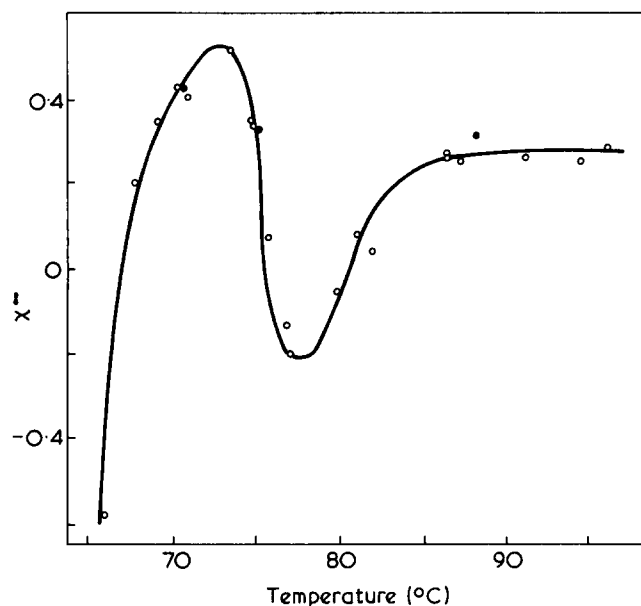


Figure 4 Interaction parameter extrapolated to zero solvent concentration, χ^∞ , vs. temperature in the poly(ethylene oxide) ($M = 5.0 \times 10^6$)/benzene system. ●, are values from gas chromatography by Chang and Bonner³ ($M = 4.0 \times 10^6$)

Values of χ^∞ in the PEO–benzene system depend greatly on temperature and polymer molecular weight at temperatures below 90°C. Such behaviour cannot be explained by usual theories of polymer solution thermodynamics. Investigations of PEO melting point⁴⁰; crystallization isotherms^{41,42}; conformation in the solid state, melt, and solution^{43,44}; and thermodynamic studies⁴⁵ have been extensive. Beech *et al.*⁴⁰ have studied the melting behaviour of PEO of narrow molecular weight distribution. They observed one melting transition for fractions of molecular weight 4000 or less and two melting transitions for samples with molecular weights from 6000 to 20 000. For example, T_m (melting point) of PEO is 65.9° and 66.7°C for $M_w = 20\ 000$, $M_w/M_n \approx 1.2$ with T_c (crystallization temperature) = 54.8°C. These melting transitions found for samples of $M_w = 10\ 000$ and 20 000 presumably

correspond to differing folded-chain morphologies, while the PEO fraction of molecular weight M_n less than 4000 crystallized in an extended-chain lamellar crystal⁴⁰.

The morphological results of Beech *et al.*⁴⁰ can be compared with the temperature dependence of the χ^∞ parameter. This behaviour is characterized by two minima: one in the vicinity of 65°C, which coincides with the melting point (65.3–68.2°C, depending on crystallinity) of the PEO ($M = 6.1 \times 10^5$)⁴⁶; and one in the range of 77° to 85°C, depending on the molecular weight of the polymer.

The values of χ^∞ in the PEO–benzene system at temperatures higher than 90°C are in the range of 0.22 to 0.30 depending on the molecular weight of polymer, and the concentration dependence of χ is negligible. It is also interesting to compare our values of χ with those of other polymer solutions. For example, the values of χ^∞ and $(\partial\chi/\partial\psi_1)^\infty$ in polyisobutylene¹⁷/benzene are 1.15 and –1.4 respectively, 0.92 and –0.9 for polyisobutylene/n-pentane¹⁹, 0.896 and –0.42 for poly(dimethyl siloxane)/benzene¹⁵, and 0.9 and –0.5 for polystyrene/methyl ethyl ketone⁹. On the other hand, the values of χ^∞ and $(\partial\chi/\partial\psi_1)^\infty$ are 0.37 and 0.18 for polystyrene/toluene⁹, 0.316 and 0.05 in PDMS/hexamethyl disiloxane¹⁵, and 0.51 and –0.14 for natural rubber/benzene, which are closer to that of the poly(ethylene oxide)/benzene system than the former systems. The small values of χ^∞ for poly(ethylene oxide)/benzene suggests that benzene is a good solvent for PEO due to the special interaction⁷ between PEO and benzene caused by charge transfer between the benzene (donor) and ether oxygen (acceptor).

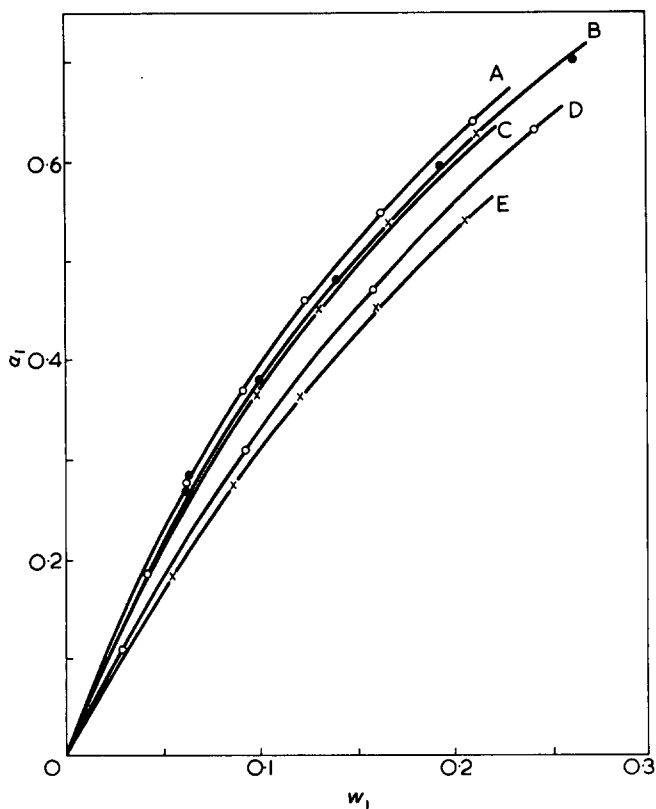


Figure 5 Comparison of activity of benzene vs. weight fraction of solvent (w_1) data in the poly(ethylene oxide)/benzene system by various methods: present method A, ($M = 5.0 \times 10^6$, 70.1°C); C, ($M = 6.0 \times 10^5$, 70.7°C); E, ($M = 1.0 \times 10^5$, 70.6°C); gas chromatographic method of Chang and Bonner³, B, ($M = 4.0 \times 10^6$, 70.6°C); vapour pressure measurement of Booth and Devoy⁷; D, ($M = 6.0 \times 10^5$, 70.0°C)

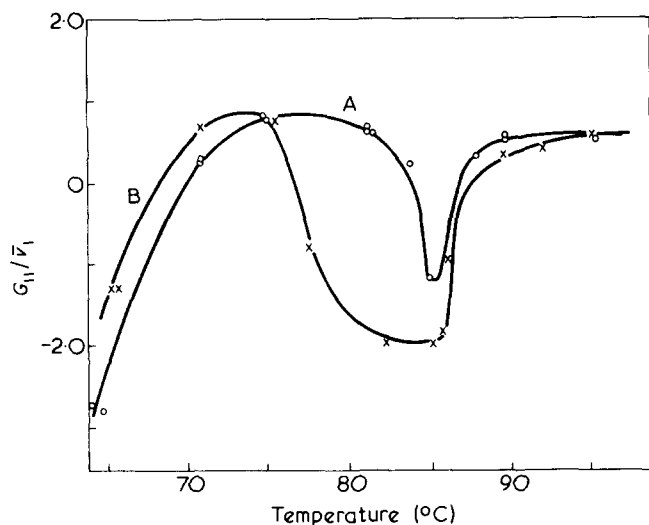


Figure 6 Ratio of clustering function of solvent (G_{11}) to partial molecular volume of solvent (\bar{v}_1) vs. temperature in the poly(ethylene oxide) ($M = 1.0 \times 10^5$, A; $M = 6.0 \times 10^5$, B)/benzene system

Zimm²⁹ developed a simplified relation between thermodynamics and the molecular distribution function for mixtures based on Kirkwood–Buff³⁰ theory and applied it to polymer solution. The relation between the activity coefficient and solvent clustering function G_{11} for systems of negligible compressibility is given by^{29,31}:

$$G_{11}/\bar{v}_1 = -\Phi_2[\partial(a_1/\Phi_1)/\partial a_1]_{P,T} - 1 \quad (9)$$

where Φ_1 is the volume fraction of solvent and \bar{v}_1 is partial molecular volume of solvent. The clustering integral G_{11} is defined by:

$$G_{11} = (1/V) \iint [F_2(i,j) - 1] d(i)d(j) \quad (10)$$

where V is the volume of system, and the molecular pair distribution function, $F_2(i,j)$, is defined by the statement that $(1/V^2)F_2(i,j) d(i)d(j)$ is the probability that the molecules i and j are each at the positions specified by the coordinates (i,j) in the coordinate range $d(i)$ and $d(j)$.

Determination of the solvent clustering function G_{11} for the PEO/benzene system by equation (9) has been carried out using the Flory–Huggins equation (6) for infinite molecular weight of polymer with segment fraction (ψ) replacing volume fraction (Φ):

$$G_{11}/\bar{v}_1 = [2\chi - (\partial\chi/\partial\psi_1)\psi_2] / [1 - 2\chi\psi_1 + (\partial\chi/\partial\psi_1)\psi_1\psi_2] \quad (11)$$

For infinite dilution of solvent ($\psi_1 \rightarrow 0$), G_{11}/\bar{v}_1 approaches $2\chi - \partial\chi/\partial\psi_1$. The calculated values of G_{11}/\bar{v}_1 at infinite dilution of solvent in PEO–benzene mixture are shown in Figures 6 and 7. The values of G_{11}/\bar{v}_1 are in the range of -1.0 to -3.0 in the vicinity of 65°C and the temperatures corresponding to the second minimum of G_{11}/\bar{v}_1 . This indicates that a benzene molecule in the PEO/benzene system at the limit of zero concentration of benzene excludes its own volume, or twice its volume, to other benzene molecules and that sorption of benzene vapour by the PEO proceeds homogeneously as in the case of an ideal mixture ($a_1/\Phi_1 = \text{constant}$, $G_{11}/\bar{v}_1 = -1$). At the melting point,

volume expansion occurs corresponding to the phase transformation from perfect crystal [$V^0(25^\circ\text{C}) = 0.813 \text{ (cm}^3/\text{g)}$] to liquid [$V^0(25^\circ\text{C}) = 0.891 \text{ (cm}^3/\text{g)}$]⁴⁷. The degree of volume expansion in the real, crystalline polymer depends on the crystallinity of the polymer. Therefore, extra sorption sites and space would be formed at temperatures in the vicinity of the melting point through the expansion of polymer and also enlargement of the amorphous region.

On the other hand, the values of G_{11}/\bar{v}_1 are in the range of 0.5 to 1.0 in the vicinity of 77°C for PEO with $M = 1.0 \times 10^5$, 73°C for PEO with $M = 6.0 \times 10^5$, and 72°C for PEO with $M = 5.0 \times 10^6$, and at higher temperatures than about 90°C for all PEO samples, as is shown in Figures 6 and 7. These values of G_{11}/\bar{v}_1 suggest that the concentration of benzene molecules is higher than average in the neighbourhood of a benzene molecule and that benzene molecules cluster together. Zimm explained the situation as follows. The first solvent molecules to enter the polymer structure loosen the structure, and make it easier for subsequent molecules to enter in the neighbourhood of the first than to enter at unfavourable sites on the polymer.

We can also calculate the solvent clustering function for the Langmuir adsorption isotherm:

$$a_1 = \frac{cN_1}{(N_s - N_1)} = cv_s\Phi_1/(\bar{v}_1\Phi_2 - v_s\Phi_1) \quad (12)$$

where c is a constant, N_1 is the number of molecules of component 1 of partial molecular volume \bar{v}_1 , N_s is the number of 'cells' or adsorption sites in the polymer, v_s is the volume of adsorbing material per site, and Φ_2 is the volume fraction of adsorbing material in the mixture. The calculation of equation (9) by the use of equation (12) leads to the result³¹:

$$G_{11}/\bar{v}_1 = -2 - v_s/v_1 + (1 + v_s/v_1)\Phi_1 \quad (13)$$

The clustering function of the solvent for the Langmuir adsorption isotherm in the limit of $\Phi_1 = 0$ gives $-(2v_1 + v_s)$, which means that the excluded volume is twice the volume of the adsorbed molecule plus the site on which it is adsorbed.

With the above background, we examine the two types of concentration dependence of Γ_1 in Figure 1 by use of the

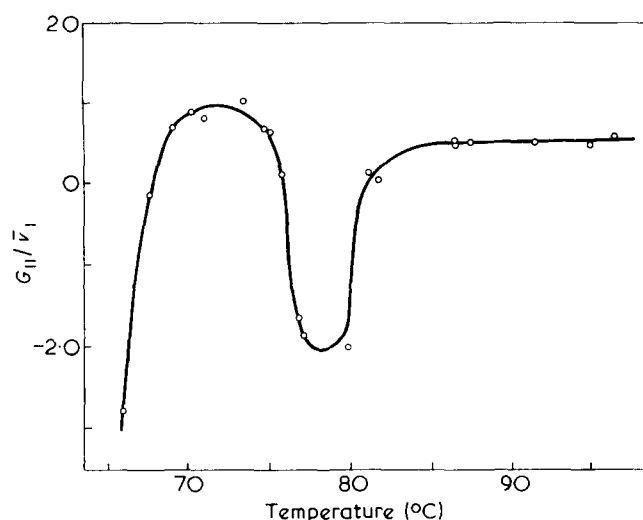


Figure 7 Ratio of clustering function of solvent (G_{11}) to partial molecular volume of solvent (\bar{v}_1) vs. temperature in the poly(ethylene oxide) ($M = 5.0 \times 10^6$)/benzene system

clustering function of the solvent. The negligibly small dependence of Γ_1 on concentration and small values of Γ_1 corresponding to large values of ψ_1 lead to $G_{11}/\bar{v}_1 = -1.0$ to -3.0 , which expresses the case of ideal solution or Langmuir adsorption. The χ parameter, corresponding to $G_{11}/\bar{v}_1 = -1.0$ to -3.0 , increases rapidly with an increase of concentration, as shown in *Figure 2*. This suggests that the solubility of benzene in PEO becomes better as zero solvent concentration is approached and worse as the amount of sorption or coverage of sites in the polymer increases. In this case, there would be a larger number of sites on the polymer to allow the random occupation of sites.

The decrease of Γ_1 with an increase of ψ_1 leads to $G_{11}/\bar{v}_1 = 0.5$ to 1.0 , which corresponds to the case of sorption by clustering of solvent molecules. The large value of Γ_1 in the vicinity of $\psi_1 = 0$ indicates few sites on the polymer as compared to the former case. The constant value of χ against concentration corresponding to $G_{11}/\bar{v}_1 = 0.5$ to 1.0 also reflects the process of clustering of solvent molecules. From these examinations one can say that the sorption of vapour strongly depends on the number of sites on the pure polymer, which would be related to the morphology³⁵ and configurations of polymer chains in the amorphous state³⁴ or crystalline state.

CONCLUSIONS

We have determined the activity coefficient of benzene in poly(ethylene oxide) over the temperature range of 64°C to 97°C with polymer molecular weights of 1.0×10^5 , 6.0×10^5 , and 5.0×10^6 g/g mol by the piezoelectric sorption method. We observed that the polymer-solvent interaction parameter χ for infinite dilution of solvent is strongly dependent on temperature and on the molecular weight of polymer at temperatures higher than melting point (65°C) and below 90°C . The χ parameter at temperatures higher than 90°C is almost constant with temperature and molecular weight of polymer, which is consistent with the χ parameter in the Flory-Huggins theory derived from a random coil model. Second minima of χ^∞ are observed at 85°C for samples with molecular weight 1.0×10^5 , 84°C for samples with molecular weight 6.0×10^5 , and 77°C for the sample with molecular weight 5.0×10^6 . These minima of χ^∞ presumably correspond to some kind of transition similar to melting transition accompanied by the change to random coil configurations of the polymer chains.

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