

Thermodynamics of the Mixture Poly(Ethylene Oxide)/ Toluene

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SUMMARY

Excess volumes at 60°C for concentrated mixtures of poly(ethylene oxide) and toluene have been determined. The volume change of mixing is negative, amounting to -0.59% of the total volume at the segment fraction $\phi_2=0.5$. This result has been used in adjusting the energy parameter $X_{12}=1.8 \text{ cal cm}^{-3}$, from which theoretical values of the residual chemical potential parameter χ , partial molar enthalpies and entropies at different concentrations can be evaluated through the Flory-Prigogine-Patterson theory. Solvent activities for moderately concentrated solutions have been measured by vapour pressure osmometry at 42° and 70°C. Inverse gas chromatography was also used in order to obtain the χ value at $\phi_2=1$. The reduced partial molar excess enthalpy κ was calculated from the experimental viscosity-temperature coefficient. Experimental and theoretical values have been compared.

INTRODUCTION

The statistical thermodynamics of polymer solutions is nowadays based on the theory formulated by Flory and co-workers (FLORY 1965b) (EICHINGER and FLORY 1968) and by PATTERSON (1967) applying the ideas of PRIGOGINE (1957) and his school. This theory, designated as the equation-of-state theory (EST), arises from the incapacity of the Flory-Huggins theory (FH) (FLORY 1953a) in explaining experimental singularities of such mixtures like excess volume over the additive one, the appearance of both upper critical solution temperature (UCST) and lower critical solution temperature (LCST), the dependence of the excess thermodynamic magnitudes on the concentration and the departure of the molar entropy from the solely combinatorial one, calculated assuming the model of a rigid lattice for the solution as Flory and Huggins did.

Different experimental techniques can be used in determining activity coefficients of the solvent in polymer solutions (RABEK 1980). In this paper we report data from vapour pressure osmometry (VPO), which has been employed rarely (BROWN 1967). Given the intrinsic limitations of VPO in obtaining data at high concentrations, we have used inverse gas chromatography as an experimental method capable of providing values of thermodynamic magnitudes at very high concentrations of the polymer (GRAY 1977). In the other hand, the temperature coefficient of the intrinsic viscosity has been used in determining the reduced partial molar excess enthalpy K .

EXPERIMENTAL

*Material and Methods

Different samples of POE were obtained from Polysciences Inc., Warrington, USA. After a slight fractionation in the benzene/isooctane mixture, three fractions were selected. Viscosity average molecular weights were calculated from viscometric equations (BEECH and BOOTH 1969) (SADRON and REMPP 1958) taken into account the very different molecular weights selected. The \bar{M}_v values were 5,200 364,700 and 759,700 respectively. The first fraction was used in VPO, the second in chromatography and the third one in viscometry.

The osmometer was a KNAUER, provided with thermistors covering the range 25-70°C. Experimental details for accurate measurements were described elsewhere (BILLINGHAM 1977). The calibrating substance was Benzil.

Viscosities were measured by means of Ubbelohde capillar viscometers. Temperatures were controlled to $\pm 0.01^\circ\text{C}$. Excess volume measurements were carried out with a pycnometer, previously calibrated with distilled, air-free water at 60°C. The gas chromatograph was a dual column apparatus (Perkin Elmer 3920 B) equipped with a flame ionization detector. The flow rate of the N_2 carrier gas was measured with a soap-bubble flowmeter and corrected for column pressure drop and water vapour content, being 19 mls/min. at 273°K. The column pressure drop was read with a cathetometer. The column, a 0.25 inch. stainless-steel tubing, was filled with 1.099 g. of POE polymer coated in 80-100 mesh Fluoropack-80 with a loading of 7.83%.

**Equation of state parameters

For the purpose of evaluating thermodynamic properties of the mixture, characteristic values of the pure components were calculated at 60°C. The three characteristic parameters v^* , T^* and p^* may be evaluated from equation of state data for the pure components; density, thermal expansion coefficient (α) and thermal pressure coefficient (γ) provide the necessary data. Values of these magnitudes for POE were taken from BOOTH and DEVOY (1971).

Data for toluene were encountered in bibliography (MC GLASHAM and POTTER 1962) (HANDBOOK OF CHEMISTRY AND PHYSICS 1976). Reduced and characteristic parameters for each component can be calculated with the equations (EICHINGER and FLORY 1968)

$$\bar{v}_i^{1/3} - 1 = (\alpha_i T / 3) (1 + \alpha_i T) \quad (1)$$

$$v_{sp,i}^* = v_{sp,i} / \bar{v}_i \quad (2)$$

$$p_i^* = \gamma_i T \bar{v}_i^2 \quad (3)$$

$$T/T_i^* = \bar{v}_i = (\bar{v}_i^{1/3} - 1) / \bar{v}_i^4/3 \quad (4)$$

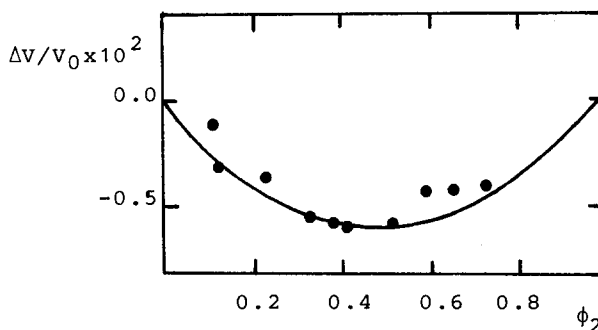


Figure I.-The excess volume at 60°C for POE/toluene. The circles are experimental points; the curve has been calculated from theory.

Reduced volumes and characteristic magnitudes at 60°C for pure components of the mixture are collected in Table I.

TABLE I
Characteristic parameters for POE and toluene at 60°C.

	<u>Toluene</u>	<u>POE</u>
v	1.2972	1.2132
v_{sp}^* ($\text{cm}^3 \text{g}^{-1}$)	0.9291	0.7536
p^* (cal cm^{-3})	125.52	160.76
T^* ($^{\circ}\text{K}$)	5,203	6,478

RESULTS AND DISCUSSION

The excess volumes at 60°C are negative as Figure I shows, where the experimental values are plotted against the segment fraction ϕ_2 , defined as

$$\phi_2 = m_2 v_{sp,2}^* / (m_1 v_{sp,1}^* + m_2 v_{sp,2}^*) \quad (5)$$

where m_i are the quantities (in grams) of the components. The maximum excess was found in the vicinity of $\phi_2 = 0.5$, this excess being -0.59% over the total volume.

Equations for calculating activity coefficients of the solvent by VPO are given elsewhere (BROWN 1967). Experimental values of the reduced chemical potential χ , were obtained from the equation

$$\ln a_1 = \ln(1-\phi_2) + (1-1/x) \phi_2 + \chi \phi_2^2 \quad (6)$$

where x is the number of segments per polymer molecule having the characteristic volume of the solvent, i.e.

$$x = M_2 v_{sp,2}^* / M_1 v_{sp,1}^* \quad (7)$$

Equation (6) has the same form that in the FH theory, but now $RT\chi\phi_2^2$ contains the different contributions affecting the partial molar free energy, apart from the solely combinatorial. The values of χ at different concentrations are plotted in Figure II. Our results provide an experimental value of 0.39 at infinite dilution ($\phi_2=0$).

An additional experimental point, at $\phi_2=1$, was obtained by inverse gas chromatography at 70.2°C. We have preferred to carry out measurements at this temperature because the melting point of POE is approximately 65°C and at 60°C the data obtained could be not entirely representative of the situation in the solution. χ can be obtained from the equation (GRAY 1977)

$$\chi = \ln(273.2 R v_{sp,2}^* / p_1^0 V_g^* V_1^*) - |p_1^0 / RT(B_{11} - V_1)| - 1 \quad (8)$$

where p_1^0 is the vapour pressure of the pure solvent, V_1^* the characteristic molar volume of the solvent, B_{11} its second virial coefficient and V_g^0 the specific retention volume. The V_g^0 value measured at 70.2°C was 174.4 cm³ which is in excellent agreement with the interpolated in the CHENG and BONNER (1974) data in the range 50-150°C. The reduced chemical potential so calculated was 0.498. As Figure II shows, a small positive deviation can be expected when we go from 70.2° to 60°. Consequently we can report a value of c.a. 0.50, which is also drawn in Figure II at $\phi_2=1$.

At the same time, this little variation in the values between 42° and 70°C makes very problematic the possibility of obtaining accurate values of entropies and enthalpies of dilution from the data of chemical potentials at two temperatures. In spite of this limitation, we have calculated entropies and enthalpies at 60°C. As the experimental values of $\overline{\Delta H}_1 / RT\phi_2^2$ and $\overline{\Delta S}_1 / R\phi_2^2$ do not show a definite increasing or decreasing tendency with the segment fraction, we decided to average the available data in order to obtain tentative values of such magnitudes. The results, 0.02 and 0.34 respectively, are subjected to large uncertainties (± 0.06 and ± 0.10).

We have measured the temperature coefficient of the intrinsic viscosity $d \ln[\eta] / dT$ as an alternative way for a reliable estimation of the reduced partial molar excess enthalpy $\kappa = -T(d\chi/dT)$. As is well established, a knowledge of $d\chi/dT$ is a condition for determining the temperature

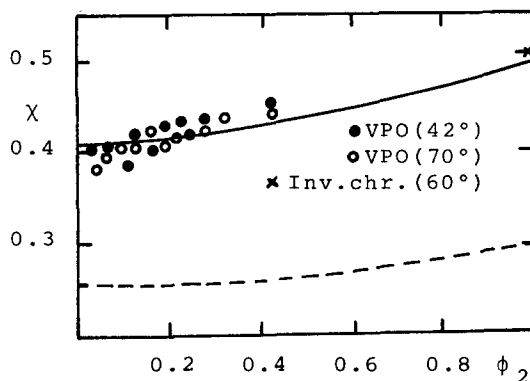


Figure II.-The reduced residual chemical potential against segment fraction. The points are experimental. The curves are calculated from the theory (see text).

coefficient of the unperturbed dimensions by means of the equation (FERNANDEZ-BERRIDI et al. 1980)

$$d \ln \langle r^2 \rangle_0 = (2\alpha_\eta^3/3) d \ln [\eta] / dT - 2/3 (\alpha_\eta^3 - 1) \left\{ (2\alpha_2 - \alpha_1) - (1/2 - X)^{-1} dX/dT \right\} \quad (9)$$

where α_η is the expansion coefficient of the coil. The temperature coefficient of the unperturbed dimensions seems to be well established (FLORY 1969c), the accepted value for POE being $0.23 \times 10^{-3} \text{K}^{-1}$. The temperature coefficient of the intrinsic viscosity was $-1.3 \times 10^{-3} \text{K}^{-1}$ for the high molecular weight used. BEECH and BOOTH (1969) have measured intrinsic viscosities in the theta solvents isobutyl ketone and diethylenglycol diethyl ether at 50°C . Therefore, we can obtain the expansion coefficient at 50°C as

$$\alpha_\eta^3 = [\eta] / [\eta]_\theta \quad (10)$$

with our data in toluene. With these results and equation (9) we have obtained a $dX/dT = 3.4 \times 10^{-4}$ corresponding to $\kappa = -0.11$, somewhat lower than that obtained by VPO. However, it can be argued that, because of the important difference in the molecular weights used in the experiments, the discrepancy could arise from the hydrogen bonds involving the hydroxyl groups which terminate the molecules in both samples. The consideration of these bonds will result in a substantial positive contribution to $\overline{\Delta H}_1$ for the low molecular weight sample.

Comparison with the theory

We can compare the experimental results with the theoretical magnitudes predicted by the Flory-Prigogine-Patterson theory (EICHINGER and FLORY 1968). The basic

equations referring to excess volumes are,

$$\tilde{v}-\tilde{v}_0/\tilde{v}_0 = (v-v_0/v_0)^{\text{exp}} = \tilde{v} - (\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2) / (\phi_1\tilde{v}_1 + \phi_2\tilde{v}_2) \quad (11)$$

$$T^* = T \tilde{v}^{4/3} / (\tilde{v}^{1/3} - 1) \quad (12)$$

$$1/T^* = (\phi_1 p_1^*/T_1^* + \phi_2 p_2^*/T_2^*) / (\phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12}) \quad (13)$$

$$\theta_2 = (s_2/s_1)\phi_2 / \phi_1 + (s_2/s_1)\phi_2 \quad (14)$$

where \tilde{v} and T^* are magnitudes of the mixture, θ_2 is the so-called site fraction of the polymer; s_2/s_1 is the ratio between a polymer segment surface, having the same characteristic volume as the solvent, and the surface of the solvent molecule. We have calculated s_2/s_1 as BOOTH and DEVOY (1971) did for the POE/benzene mixture, and the result was 0.86.

X_{12} characterizes the interactions between neighbouring polymer/solvent pairs. As we will show, this parameter appears in all the excess thermodynamic magnitudes and must be adjusted to match any one of the experimental measured quantities. The excess volume has been selected from consideration of the accuracy with which this magnitude can be determined. The full curve in Figure I has been calculated from theory with $X_{12} = 1.8 \text{ cal cm}^{-3}$ and the value of s_2/s_1 specified above.

The reduced excess chemical potential was calculated according to the theory with the equation

$$\chi = (p_1^* \tilde{v}_1^* / RT \phi_2^2) \{ 3T_1 \ln | (\tilde{v}_1^{1/3} - 1) / (\tilde{v}^{1/3} - 1) | + (\tilde{v}_1^{-1} - \tilde{v}^{-1}) \} + (V_1^* X_{12} / \tilde{v}) \theta_2^2 / RT \phi_2^2 \quad (15)$$

The dashed curve, which appears in Figure II, corresponds to this equation. More accurate agreement can be achieved by a selection of $X_{12} = 4$, but this would lead to a higher, not reliable value of κ and further discrepancies in the measured excess volumes. Following the suggestion of EICHINGER and FLORY (1968), we have introduced an entropy interaction parameter Q_{12} for suppressing discrepancies between experimental and theoretical values of χ . The required value of Q_{12} was $-0.0046 \text{ cal cm}^{-3} \text{ }^\circ\text{K}^{-1}$. Figure III shows the reduced partial molar enthalpy, calculated from the theory by means of the equation

$$\bar{\Delta H}_1 = p_1^* \tilde{v}_1^* | (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + (\alpha T / \tilde{v}) (T_1 - T) / T | + (V_1^* X_{12} / \tilde{v}) (1 + \alpha T) \theta_2^2 \quad (16)$$

where α is the thermal expansion coefficient of the mixture, calculated from \tilde{v} , according to equation (1). At infinite dilution, $\kappa = 0.07$ is higher than both viscometric and osmometric measurements, although as we have mentioned, the small variations of χ with temperature and the intrinsic complications in determining temperature coefficients can introduce large errors.

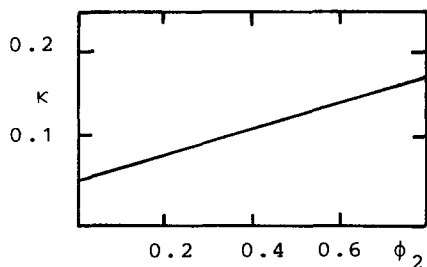


Figure III.-The reduced partial molar enthalpy against the segment fraction, according to the theory.

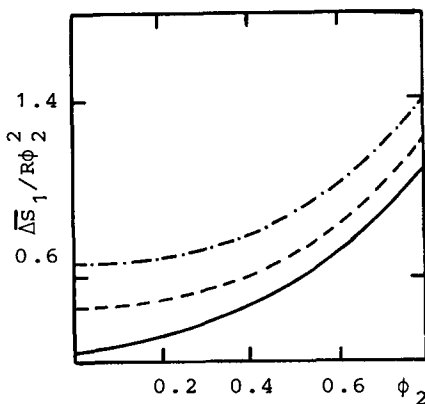


Figure IV.-The reduced partial molar entropy against segment fraction. Symbols are explained in the text.

Figure IV shows the influence of the different factors affecting the partial molar entropy. The dot-dashed curve represents the combinatorial contribution

$$(\overline{\Delta S}_1)_{\text{comb.}} = -R \left[\ln(1-\phi_2) + (1-1/x)\phi_2 \right] \quad (17)$$

The dashed curve summarizes combinatorial plus residual entropy (\overline{S}_1^R), calculated according to the EST as

$$\overline{S}_1^R = -p_1^* v_1^* \left\{ (3\hat{T}_1/T) \ln \left| (\hat{v}_1^{1/3} - 1) / (\hat{v}^{1/3} - 1) \right| - (\alpha/\hat{v}) (\hat{T}_1 - \hat{T}) / \hat{T} \right\} + \alpha v_1^* x_{12} \theta_2^2 / \hat{v} \quad (18)$$

The full curve includes the Q_{12} term. With the same cautions above mentioned, the value at $\phi_2=0$ $\overline{\Delta S}_1/R\phi_2^2=0.27$ seems to be in good agreement with our experimental results from VPO.

In analyzing the above reported data for the POE/toluene mixture, we can conclude that approximately equal contributions are made to the reduced residual chemical potential from three sources: a) equation of state terms of the pure components, b) contact energy X_{12} and c) contact entropy Q_{12} . For instance, at $\phi_2=0.1$, the corresponding contributions to χ from these sources are 0.134, 0.137 and 0.150. The contributions to $\overline{\Delta S}_1$, which arise from the first and the third are both negative and of significant magnitude, giving a total entropy of mixing much lower than the value given by the combinatorial lattice expression of the FH theory. Finally, the adjustment of X_{12} in using the theoretical expression for excess volumes provides a curve which reproduces the experimental points.

Equation-of-state theory seems to be successful for the

polar system studied. As known, this theory was essentially developed to explain thermodynamic phenomena in nonpolar systems and it has not been modified for taking account of the dipolar effects in polar mixtures. As SUGAMIYA et al. (1974) have argued, the success with polar systems may be due to the fact that the polar effect is implicitly included in the exchange entropy as well as in the intermolecular energy. Further investigations are being carried out with polymers in poor solvents where a more extended dependence of χ with T can be expected allowing a more reliable estimation of enthalpies and entropies.

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