# Gas–liquid chromatography study of poly(ethylene oxide)–solvent interactions: estimation of polymer solubility parameter

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(Received 14 September 1982; revised 12 January 1983)

The thermodynamics of the interactions in the liquid state (70°–150°C) between poly(ethylene oxide) ($\bar{M}_n = 10^4$) and 32 solvents covering a wide range of structure and polarity (from n-hexane to 2,2,2-trifluoroethanol) were studied by gas–liquid chromatography. The regular solution theory, in spite of its well known limitations, does allow a very self-consistent interpretation of all the data for the systems characterized by a positive Flory parameter $\chi$, including systems of poly(ethylene oxide) and a self-associated alcohol where specific hydrogen bonding is well known. The polymer solubility parameter $\delta_2$ ($\delta_2 = 9.6 \pm 0.1$ (cal cm$^{-3}$)$^{0.5}$ at 70°C) and its temperature dependence are easily derived with good accuracy.
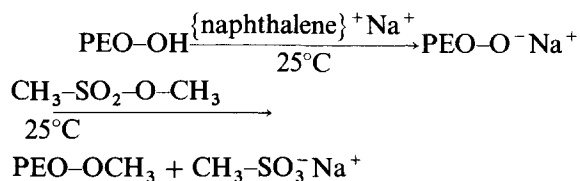
## INTRODUCTION

The gas–liquid chromatography (g.l.c.) study of the thermodynamics of polymer–solvent interactions in the liquid state at probe infinite dilution has been the subject of outstanding developments within the last decade[1,2]. Investigations were restricted in most cases to non-polar systems for which current polymer–solvent theories actually apply, especially the Hildebrand solubility parameter approach[3]. However, in spite of their wide occurrence and of their definite technological and theoretical interest, only a few studies have so far been devoted to polar polymeric systems such as poly(ethylene glycol)[4], polyacrylates[5], vinyl chloride–vinyl acetate, ethylene–vinyl acetate or butadiene–acrylonitrile copolymers[6,7].

In the present work, the thermodynamics of interactions between poly(ethylene oxide) (PEO) and a wide range of solvents (polar or apolar, protic or aprotic), leading eventually to specific dipolar or hydrogen bond interactions with the polyether chain $(CH_2-CH_2-O)_n$, will be discussed critically within the framework of the Hildebrand solubility parameter theory. This allows a test of the validity of this popular approach on a well defined polymer representative of weakly polar systems which are not expected strictly to obey the model of the regular solution theory.

## EXPERIMENTAL

### Materials

The terminal primary alcohol functions of purified PEO H-10000 from Hoechst ($\bar{M}_n = 10\,700$, $\bar{M}_w/\bar{M}_n = 1.07$) were methylated in homogeneous tetrahydrofuran solution according to the following scheme[8]:

$$PEO-OH \xrightarrow[25°C]{\{naphthalene\}^+Na^+} PEO-O^-Na^+$$

$$CH_3-SO_2-O-CH_3 \atop \xrightarrow{25°C}$$

$$PEO-OCH_3 + CH_3-SO_3^-Na^+$$

This procedure is repeated twice and less than 3% of the original OH groups remain unchanged, as checked by their potentiometric titration after previous conversion to carboxylic functions according to the literature[9].

### Apparatus, preparation of columns and experimental procedure

These were the same as described before[10]. The PEO samples were deposited from benzene solution on glass beads of specific surface area 0.016 m$^2$ g$^{-1}$, previously treated with hexamethyldisilazane (HMDS). After drying, the coated support was packed into 0.25 inch stainless-steel tubing. Two columns containing 0.206 and 0.119 g of polymer respectively were used.

Preliminary experiments showed that, in the liquid state ($t > 70°C$), the influences of column loading within the range 0.6–1.2% and of flow rate of the gas vector within the range 4–15 ml min$^{-1}$ are negligible. On the other hand, the retention times were a function of the amount of solute injected only for alcohols and for temperatures lower than 100°C; extrapolations to zero amount of solute were made systematically whenever necessary.

## RESULTS AND DISCUSSION

### Data reduction

The retention times were converted to the specific

retention volumes corrected to 0°C, $V_g^\circ$, in the classical way[1]. Various thermodynamic parameters, including the weight fraction activity coefficient $\Omega^\infty$ and the Flory–Huggins parameter $\chi$, were calculated for a number of solvents and non-solvents of PEO according to the equation derived by Patterson *et al.*[11]:

$$\ln\Omega^\infty = \ln\left(\frac{273.2R}{P_1^\circ V_g^\circ M_1}\right) - \frac{P_1^\circ}{RT}(B_{11} - V_1) \qquad (1)$$

$$\chi = \ln\Omega^\infty - \ln\left(\frac{v_1}{v_2}\right) - 1 + \frac{M_1 v_1}{M_2 v_2} \qquad (2)$$

where subscripts 1 and 2 refer to the probe and the polymer respectively, $M$ is the molecular weight, $P^\circ$ is the saturation vapour pressure at temperature $T$, $V$ and $v$ are the liquid state molar volume and specific volume respectively and $B_{11}$ is the gas state second virial coefficient at $T$. The enthalpic contribution $\chi_H$ to the Flory parameter $\chi$ ($\chi = \chi_H + \chi_S$) may be deduced from the $\Omega^\infty$ variations versus temperature:

$$\chi_H = -\frac{T \partial\Omega^\infty}{\Omega \, \partial T} \qquad (3)$$

The partial molar heat of mixing $\overline{\Delta H_1^\infty}$ (heat of dilution) of the solute at infinite dilution in the polymer, relative to that in the pure liquid state, is directly deduced from $\chi_H$ values:

$$\overline{\Delta H_1^\infty} = RT\chi_H \qquad (4)$$

For the derivation of the various thermodynamic parameters, solute vapour pressures were computed from the Antoine equation, selecting the corresponding constants from the Dreisbach or Boublik compilations[12,13], except for 2,2,2-trifluoroethanol[14]. Solute molar volumes $V_1$ were obtained from Dreisbach and from other sources, especially Timmermans[15]; in a few cases, their values were extrapolated to the required temperature range from literature data. Second virial coefficients $B_{11}$ were derived from the correlation given by O'Connell and Prausnitz[16]. PEO specific volume $v_2$ was calculated according to the equation[10]:

$$v_2 (\text{ml g}^{-1}) = 0.9217 + 6.9 \times 10^{-4}(t - 70), \quad 70° < t < 100°C$$

Assuming no volume change on mixing, the Hildebrand–Scatchard equation is of the form[17]:

$$\overline{\Delta H_1} = V_1(\delta_1 - \delta_2)^2 \qquad (5)$$

where $\delta_1$ and $\delta_2$ are the solubility parameters of the solute and of the polymer respectively. The partial molar heat of mixing $\overline{\Delta H_1}$ is necessarily positive or zero: this is strictly valid for the mixing of liquids in which only intermolecular dispersion forces are operative.

Because of the poor accuracy of the $\overline{\Delta H_1^\infty}$ determination which requires careful g.l.c. measurements as a function of temperature, we focused our interest on the Flory interaction parameters $\chi$, which may be obtained with good precision and correlated with the Hildebrand theory according to the following relation:

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + \chi_S \qquad (6)$$

Equation (4) may be rewritten in the form:

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S}{V_1}\right) \qquad (6a)$$

Assuming that the dependence of $\chi_S/V_1$ on $\delta_1$ is negligible, the solubility parameter of the polymer, $\delta_2$, is easily derived from the slope of the linear variation of $\delta_1^2/RT - \chi/V_1$ versus $\delta_1$ for a series of well characterized probes, while the intercept leads to an estimation of the $\chi_S$ value. The required solubility parameters $\delta_1$ of the various probes were calculated at 70°C from literature values[12] of the latent heat of vaporization $\Delta H_v$ according to equation (7), which implies that the probe vapour at infinite dilution behaves as an ideal gas:

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{0.5} \qquad (7)$$

*Weight fraction activity coefficients and derived thermodynamic parameters*

The primary $V_g^\circ$ values and the calculated $\Omega_1^\infty$ parameters at 70°, 100° and 120°C for most solvents under investigation are collected in *Table 1*, and some representative variations of $\Omega_1^\infty$ *versus* temperature are plotted in *Figure 1* for n-decane, benzene, toluene and chloroform: $\chi_H$ values may be estimated with sufficient accuracy in most cases, as given in *Table 1*.

(a) Aliphatic hydrocarbons and cyclohexane lead to high $\Omega_1^\infty$ and $\chi_H$ values, as expected for these non-solvents of PEO. Moreover, they are in very good agreement with those obtained by Leung[18] for the systems PEO 2000–n-heptane and n-decane at 66.7°C.

(b) For aromatic hydrocarbons, $\Omega_1^\infty$ progressively increases as expected when going from benzene to toluene and ethylbenzene. For benzene, the best solvent, $\chi = 0.135$ at 70°C and a partial molar heat of mixing at infinite dilution $\overline{\Delta H_1^\infty}$ of $-430 \pm 100\,\text{cal mol}^{-1}$ may be derived from its negative $\chi_H$ value. Booth and Devoy[19] have measured by a static method at 57.9°C $\chi_{\Phi_{1\to0}} \simeq 0.14$ and $\overline{\Delta H_1} = -220 \pm 40\,\text{cal mol}^{-1}$, values quite compatible with our results. Chiang and Bonner[20] however, obtained weak and positive $\overline{\Delta H_1^\infty}$ values by g.l.c. which are a decreasing function of temperature: the low accuracy for the determination of very weak $\overline{\Delta H_1^\infty}$ (ref. 21, p. 166) may contribute only partly to the observed differences which remain to be elucidated.

(c) For ethers, which may be considered in a first approach as low molecular weight model compounds of PEO, solute–PEO interactions are weaker for dimethoxyethane than for bis(2-methoxyethyl)ether and dioxan which are characterized by a nearly athermal dissolution process at 100°C ($\overline{\Delta H_1^\infty} \sim 0$).

(d) Chloroform leads to strongly negative $\chi$ and $\chi_H$ values, suggesting specific interactions with PEO. Possible hydrogen bonding between $CHCl_3$ considered as a weak hydrogen bond C–H donor and the hydrogen bond acceptor polyether chain seems very reasonable[22] and could be preferred to charge transfer complexes initially put forward and then critically discussed (ref. 21, p. 258).

(e) The positive values $\overline{\Delta H_1^\infty} = 1.43$ and 0.95 kcal mol$^{-1}$

Table 1    Specific retention volumes $V_g^o$ (ml g$^{-1}$) and thermodynamic parameters $\Omega_1^\infty$ and $\chi H$ for some probe–PEO systems at various temperatures

| Probe | 70°C | | | 100°C | | | 120°C | |
|---|---|---|---|---|---|---|---|---|
| | $V_g^o$ | $\Omega_1^\infty$ | $\chi H$ | $V_g^o$ | $\Omega_1^\infty$ | $\chi H$ | $V_g^o$ | $\Omega_1^\infty$ |
| n-Heptane | 17.87 | 31 | 2.2 | 8.44 | 26.8 | | 5.46 | 24.6 |
| n-Decane | 134.6 | 47 | 4.5 | 50.6 | 33.4 | 3.2 | 28.62 | 28.2 |
| n-Dodecane | | | | 124.6 | 53.1 | | 54.1 | 50.6 |
| Benzene | 100.0 | 4.06 | −0.6 | 40.20 | 4.26 | −0.4 | 23.64 | 4.44 |
| Toluene | 192.6 | 4.73 | −0.4 | 71.7 | 4.86 | −0.2 | 40.32 | 4.90 |
| Ethylbenzene | | | | 117.0 | 5.45 | ~0 | 63.60 | 5.43 |
| Cyclohexane | 22.92 | 16.8 | 2.8 | | | | | |
| Chloroform | 162.1 | 0.94 | −3.5 | 57.43 | 1.20 | −2.9 | 31.40 | 1.41 |
| Acetonitrile | 149.3 | 5.62 | | 56.3 | 6.23 | −1.5 | 31.9 | 6.78 |
| 1,4-Dioxan | 221.1 | 3.34 | | 81.96 | 3.35 | ~0 | | |
| 1,2-Dimethoxyethane | 80.43 | 6.17 | | 31.41 | 6.90 | −0.9 | | |
| Bis(2-methoxyethyl)ether | | | | 318.6 | 3.70 | ≤0 | 14.82 | 3.84 |
| Ethyl acetate | 62.7 | 5.18 | | 25.64 | 4.96 | 0.3 | | |
| Pyridine | | | | 161.1 | | | 85.2 | |
| 1-Propanol | 175.5 | | 2.1 | 58.58 | 5.90 | | 30.94 | 5.56 |
| 2-Propanol | 78.3 | | 1.4 | 28.68 | 7.13 | 1.2 | | |
| 2,2,2-Trifluoroethanol | 494.3 | 1.74 | −2.8 | 127.6 | | | | |
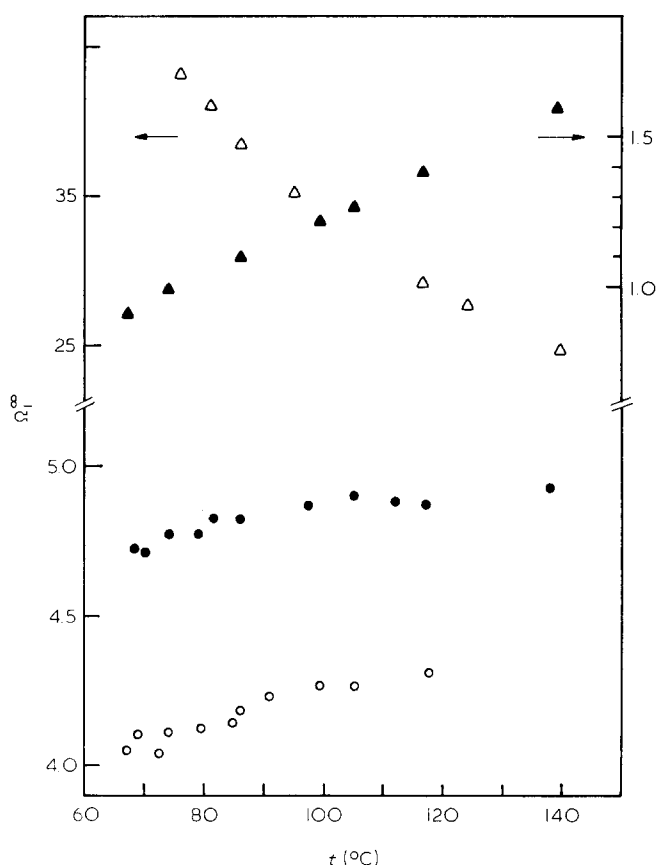


Figure 1    Temperature dependence of $\Omega^\infty$ for various probe–PEO systems: ○, benzene; ●, toluene; ▲, chloroform; △, n-decane

for PEO–1-propanol and 2-propanol respectively suggest that self-association of the alcohols prevails over PEO–alcohol hydrogen bonding interactions. However, the negative value $\overline{\Delta H}_1^\infty = -1.91$ kcal mol$^{-1}$ observed for PEO–trifluoroethanol shows that polymer–probe interactions are dominating as expected for such a fluorinated alcohol well known for its very strong hydrogen bond donor properties and its low self-association[14]. As already noticed for low molecular weight compounds[23]

and recently re-emphasized for polymeric systems such as poly(n-isopropyl acrylamide)–n-butanol[24] and poly(ethylene glycol)–ethanol[4] studied by g.l.c., the experimental partial molar heat of mixing of self-associated probes and hydrogen bond acceptor solvents or polymers should be corrected for self-association of the probe to give a physically significant picture of solute–solvent hydrogen bonding interaction. Murakami et al.[25] have measured the heats of solution of various alcohols in a non-polar solvent like n-hexane by calorimetry. Assuming with these authors that the values extrapolated to zero alcohol concentration afford a good estimate of the enthalpies of self-association $\Delta H_{sa}$ of about $5.7 \pm 0.2$ kcal mol$^{-1}$ for most of the alcohols investigated, the crude experimental $\overline{\Delta H}_1^\infty$ values may be corrected in a first approach according to:

$$\overline{\Delta H}_1(\text{alcohol} - \text{PEO}) =$$
$$= \overline{\Delta H}_1^\infty(\text{self-associated alcohol} - \text{PEO}) - \overline{\Delta H}_{sa}$$

The partial molar heats of mixing are thus decreased to the following negative values: $\overline{\Delta H}_1^\infty = -4.3$, $-4.7$ and $-7.6$ kcal mol$^{-1}$ for n-propanol, 2-propanol and trifluoroethanol respectively.

The solubility parameter approach

In order to give a wider experimental basis for the interpretation of the PEO–probe interactions, besides our measurements, we have taken into account a number of literature results.

(a) Chang and Bonner[26] obtained data with a very high molecular weight PEO sample ($\overline{M}_n = 4 \times 10^6$) within the temperature range 70°–150°C: for some common probes their results are in good agreement with our data.

(b) Klein and Jeberien[27] obtained data on a PEO sample of molecular weight $\overline{M}_n = 10\,800$ at a single temperature of 70.2°C: we corrected their values for gas-phase imperfection and found that they are in good agreement with our results for common probes.

All the $\chi$ values we derived from the literature and from our measurements are collected in Table 2, together with the solubility parameter values $\delta_1$ of the probe calculated at 70°C. Critical analysis of the results may suggest the following comments.

Table 2 Probe solubility parameters $\delta_1$ and Flory parameters $\chi$ for solute–PEO systems at 70°C

| Solute | $\delta_1$ (cal cm$^{-3}$)$^{0.5}$ | $\chi$ (exp. values) Galin (this work) | Bonner[26] | Klein[27] | $\chi$ (recalc. values, eq.(6)) |
|---|---|---|---|---|---|
| 1 n-Heptane | 6.84 | 1.93 | | 1.83 | 2.06 |
| 2 n-Octane | 6.84 | 2.03 | | | |
| 3 n-Decane | 7.27 | 2.42 | | 2.18 | 2.05 |
| 4 n-Undecane | 7.37 | | | 2.15 | 2.06 |
| 5 n-Dodecane | 7.43 | 2.70 | | 2.47 | 2.13 |
| 6 Cyclohexane | 7.60 | 1.44 | | 1.66 | 0.91 |
| 7 Benzene | 8.48 | 0.14 | 0.24 | 0.11 | 0.36 |
| 8 Toluene | 8.33 | 0.29 | 0.39 | 0.27 | 0.49 |
| 9 Ethylbenzene | 8.29 | 0.41 | | | 0.58 |
| 10 o-Xylene | 8.51 | | 0.40 | 0.44 | 0.38 |
| 11 Ethyl acetate | 8.2 | 0.40 | | | 0.50 |
| 12 Butyl acetate | 8.0 | | 0.48 | | 0.66 |
| 13 Acetone | 7.6 | | 0.25 | | 0.60 |
| 14 2-Butanone | 8.3 | | 0.28 | 0.42 | 0.43 |
| 15 1,2-Dimethoxyethane | 8.0 | 0.55 | | | 0.60 |
| 16 Tetrahydrofuran | 8.45 | | 0.19 | | 0.30 |
| 17 1,4-Dioxan | 9.2 | 0.15 | | | 0.20 |
| 18 Acetonitrile | 11.17 | 0.32 | 0.21 | | 0.20 |
| 19 Nitromethane | 12.6 | −0.03 | | 0.02 | |
| 20 Pyridine | 10.6 | −0.12 | | −0.13 | |
| 21 Carbon tetrachloride | 8.00 | 0.43 | 0.61 | | 0.60 |
| 22 Chloroform | 8.56 | −0.76 | | | |
| 23 1,2-Dichlorethane | 9.17 | −0.47 | −0.26 | | |
| 24 1,1,2-Trichlorethane | 9.18 | | −0.23 | | |
| 25 Methanol | 13.5 | 0.80 | 0.52 | | 1.04 |
| 26 Ethanol | 12.0 | | | 0.65 | 0.64 |
| 27 1-Propanol | 11.0 | 0.57 | | | 0.39 |
| 28 2-Propanol | 10.5 | 0.70 | | | 0.26 |
| 29 1-Butanol | 10.4 | | 0.37 | 0.52 | 0.29 |
| 30 2-Butanol | 10.0 | | | 0.72 | 0.22 |
| 31 2,2,2-Trifluoroethanol | 11.0 | −1.4 | | | |
| 32 Water | 22.54 | 4.96* | | | 4.56 |

* Literature value[28]

As already pointed out by Gray et al.[29], the term $\chi/V_1$ is most often weak with respect to $\delta_1^2/RT$. For the aprotic good solvents of the polymer (ethers, esters, ketones), $\chi$ remains lower than 0.4 and $\chi/V_1$ is only about 4% of the $\delta_1^2/RT$ term. For these probes, the linear variations of $(\delta_1^2/RT - \chi/V_1)$ versus $\delta_1$ are not very significantly different from the parabola $\delta_1^2/RT = f(\delta_1)$ related to the pure solute, as shown in Figure 2. For non-solvents of the polymer, however, $\chi$ increases and leads to $\chi/V_1$ values as high as 20% of the $\delta_1^2/RT$ term: equation (6a) has a greater physical meaning for these probes, which are unfortunately restricted to alkanes of similar $\delta_1$ values. The same situation holds for self-associated alcohol probes and water which also show apparent high $\chi$ and high heat of dilution values, even if they are good solvents of the polymer.

Linear regression analysis of the experimental data for all the 26 solvents of positive $\chi$ values according to equation (6a) leads to $\delta_2 = 9.6 \pm 0.1$ and $\chi_s/V_1 = 0.002$, which allow the recalculation of the $\chi$ parameter as quoted in Table 2 for every probe defined by the $\delta_1$ and $V_1$ values. These recalculated values and the experimental ones are in fairly good agreement and do not differ by more than 15%. The entropic term $\chi_S$ is positive and within the range 0.2–0.5 as expected for a polymer solution for which an average value of about 0.4 is currently quoted in the literature[30,31]. It is worth pointing out that the very good correlation ($R(23$ solv.)$ = 0.9986$) derived for all the solvents of positive $\chi$ value is not improved by excluding the apparently uncorrected data

of the self-associated alcohols.

On the other hand, the value $\delta_2(70°C) = 9.6$ is in excellent agreement with that derived for PEO $\bar{M}_n = 4000$ and only five solvents (including ethanol) by Kawakami et al.[4]: $\delta_2(67°C) = 9.4$.

The temperature dependence of the solubility parameter was studied within the range 70°–150°C. The calculated $\delta_2$ values (Table 3) are a decreasing function of temperature, and their variations are in good agreement with an empirical equation of the form:

$$\frac{\partial \ln \delta}{\partial T} = -k\alpha \tag{8}$$

where $\alpha$ is the thermal expansion coefficient. The experimental $\alpha$ value[32] of $0.78 \times 10^{-3}$ leads, however, to a coefficient $k$ of $2.1 \pm 0.3$, much higher than the estimate of 1.25 suggested by Hildebrand et al.[17] for non-polar liquids. This discrepancy is not surprising, taking into account the oversimplification involved as pointed out by Hildebrand himself.

Moreover, it may be interesting to compare the $\delta_2$ value extrapolated at 25°C from g.l.c. experiments, $\delta_2 = 10.3 \pm 0.3$ (cal cm$^{-3}$)$^{0.5}$, with the value we derived from intrinsic viscosity data[33] restricted to aprotic solvents, which may be estimated to be about $9.6 \pm 0.4$ (cal cm$^{-3}$)$^{0.5}$. This good agreement for polymer $\delta_2$ values related to the two extreme composition ranges of the
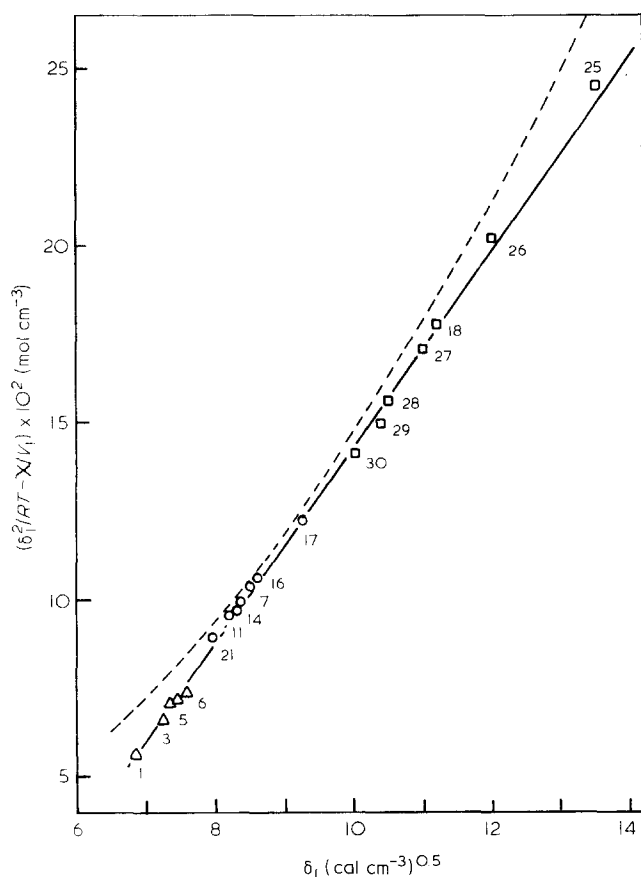
*Figure 2* Estimation of the solubility parameter $\delta_2$ of PEO at 70°C according to equation (6a): $\triangle$, n-alkanes; $\bigcirc$, aprotic solvents; $\square$, alcohols; — — —, parabola $\delta_1^2/RT = F(\delta_1)$

*Table 3* Solubility parameters $\delta_2$ of PEO at various temperatures

| $t$ (°C) | $n$ solv. | $\delta_2$ (cal cm$^{-3}$)$^{0.5}$ | Regression coeff. |
|---|---|---|---|
| 70 | 26 | 9.60 ± 0.10 | 0.9986 |
| 100 | 19 | 9.12 ± 0.16 | 0.9973 |
| 120 | 13 | 8.80 ± 0.10 | 0.9989 |
| 150 | 7 | 8.41 ± 0.10 | 0.9994 |

binary polymer–solvent system (polymer concentration →0 and ∞ respectively) is worth pointing out. Such a concordance, already observed for polyolefin, polystyrene and poly(methyl acrylate)[3,5] and for poly(vinyl acetate)[7], may probably be quite general for apolar or weakly polar systems. On the other hand, Allen et al.[32] have measured the internal pressure $P_i$ of a liquid poly(ethylene oxide) dimethylether of $\bar{M}_w \simeq 400$: $P_i = 112.3$ cal cm$^{-3}$ at 20°C. It may be assumed in a first approach[33] that $\delta_2^2 = P_i$, a very reasonable assumption for the weakly polar liquid PEO where strong specific interactions like hydrogen bonding do not contribute to its total molecular cohesion[34]. This internal pressure leads to an estimated $\delta_2$ value of 10.6 (cal cm$^{-3}$)$^{0.5}$, in good agreement with our g.l.c. value. Finally, the solubility parameter was also roughly estimated using the group contribution method. At 25°C, $\delta_2$ = 8.6, 9.7 and 10.2 (cal cm$^{-3}$)$^{0.5}$ starting from Small, Hoy and Van Krevlen data respectively[35].

## CONCLUSIONS

The thermodynamics of the interactions between PEO (selected as a model of a weakly polar polymer) and a wide

range of solvents characterized by a positive Flory parameter $\chi$ may be analysed fairly well within the framework of the Hildebrand theory: this allows an easy and accurate determination of the polymer solubility parameter and of its temperature dependence. However, in spite of its interest, such a global approach is obviously inefficient for the estimation of dispersion–cavitation forces, dipolar interactions and hydrogen bonding which contribute separately to the total polymer–solvent interactions: this would be of great interest for polar systems. Guillet et al.[6] have recently considered the popular concept of the three-dimensional polarity parameter of the solvents as the basis for such an interpretation. They conclude, however, that it is not particularly relevant for this type of problem, both from experimental and fundamental points of view. New approaches, perhaps along the same line, are obviously needed.

## APPENDIX

At the same time as we submitted our work in September 1982, we became aware of a publication by Fernández-Berridi et al. on the same topic in the latest issue (August 1982) of *Polymer*[36]. In spite of some discrepancies such as their unrealistic negative partial heat of mixing $\Delta H_1^\infty$ for n-octane and some differences in the experimental values of the activity coefficients $\Omega_1^\infty$ for a few dipolar probes (ethyl acetate, bis(2-methoxyethyl)ether)) and for self-associated alcohols, the general conclusions of both works and especially the PEO solubility parameter are in good agreement.

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