

Gas-liquid chromatography study of the thermodynamics of interactions between linear polyethylene and non-polar and polar solutes

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The thermodynamics of mixing at infinite dilution of a series of 25 low molecular weight aprotic solutes covering a broad range of polarity from n-alkanes to dimethylsulphoxide with molten linear polyethylene has been investigated by gas-liquid chromatography between 135 and 175°C. The lack of any specific solute-polymer interactions lead to partial molar free energies and enthalpies of mixing at infinite dilution, $\overline{\Delta G}_1^\infty$ and $\overline{\Delta H}_1^\infty$, are always positive. Quantitative analysis of the $\overline{\Delta G}_1^\infty$ and $\overline{\Delta H}_1^\infty$ variations with probe structure may be performed according to an empirical linear correlation $\overline{\Delta G}_1^\infty$ or $\overline{\Delta H}_1^\infty = f(\mu_1^2)$, which acknowledges the influence of solute polarity through its dipole moment μ_1 ($\overline{\Delta H}_1^\infty = (\text{KJ mol}^{-1}) = 1.43 + 0.48 (\mu_1 \times 10^{30})^2$, $R(25) = 0.95$ for instance). Alternatively, the Hildebrand-Scatchard equation, which acknowledges the influence of solute cohesion through its solubility parameter δ_1 ($\overline{\Delta G}_1^\infty N_1$ or $\overline{\Delta H}_1^\infty / V_1 = (\delta_1 - \delta_2)^2$, $R(25) = 0.90$) and which makes it possible to derive a reliable value of the PE solubility parameter: $\delta_2 = 11.3 (\text{J cm}^{-3})^{0.5}$ at 140°C for instance. These two apparently different and successful approaches may probably rest on similar physical grounds because dipolar interactions are the major factor of solute cohesion for the population under investigation.

(Keywords: gas-liquid chromatography; polyethylene; polymer-solvent interactions; solubility parameters)

INTRODUCTION

Because of its outstanding technological importance, the study of the solubility properties of low molecular weight fluids in molten polyethylene (PE) has received much attention. Fifteen years ago, Patterson *et al.*¹ stressed that for completely non-polar systems such as normal or branched alkanes at infinite dilution in molten PE, the contribution of the differences in free volume of the components to the Flory-Huggins interaction parameter χ is the major one and they have quantitatively correlated the χ variations with the thermal expansion coefficient α of the solutes. More recently a number of authors^{2,3}, starting from the principle of corresponding states, have correlated solubility properties of non-polar or weakly polar gases and volatile liquids in PE with their critical temperature and pressure and eventually with their size and shape as described by their acentric factor.

The purpose of this communication is to review the solubility properties of volatile probes in molten linear PE following three main goals. Firstly, a significant broadening of the polarity range covered by the solutes population is obtained by considering 25 aprotic solvents from non-polar n-alkanes to highly dipolar carboxylic tertiary amides or sulphoxide. Protic solvents, where self-association phenomena usually result in ambiguous interpretation of the experimental data, are avoided.

Secondly, the choice of representative thermodynamic parameters is optimized. The partial molar free energy of mixing at infinite dilution, $\overline{\Delta G}_1^\infty$, measured at

a given temperature (140°C) and the partial molar enthalpy of mixing at infinite dilution, $\overline{\Delta H}_1^\infty$, calculated between 135 and 175°C, may appear to be the best thermodynamic descriptors of the process under study. More specifically, $\overline{\Delta H}_1^\infty$ has to be preferred, for instance, to the solution enthalpy $\overline{\Delta H}_s^\infty$ which is a composite parameter where the contribution of the vaporization enthalpy of the probe $\overline{\Delta H}_v$ may be the major one ($\overline{\Delta H}_s^\infty = \overline{\Delta H}_1^\infty - \overline{\Delta H}_v$).

Thirdly, the $\overline{\Delta G}_1^\infty$ and $\overline{\Delta H}_1^\infty$ variations with probe structure are tentatively analysed emphasizing either the role of the solute polarity, (correlation analysis with its dipole moment μ and its molecular refraction MR) or the role of its cohesion (Hildebrand-Scatchard approach through the solubility parameter concept).

Gas-liquid chromatography (g.l.c.) is now well recognized as an efficient and reliable alternative to static methods for the derivation of all the thermodynamic parameters related to solute(1)-liquid polymer(2) interactions at infinite dilution and it has been systematically used throughout the experimental work.

EXPERIMENTAL

Probe molecules and polymeric stationary phase

The solvents of the best chromatography grade were used as received except dimethylformamide (DMF), dimethylacetamide (DMA) and dimethylsulphoxide

(DMSO) which were distilled under reduced pressure, over calcium hydride⁴ and stored over molecular sieves 4Å. Linear polyethylene LPE was supplied by Dupont Corp. ($\bar{M}_w = 55\,000$, $\bar{M}_w/\bar{M}_n = 4.5$, melting temperature $t_m = 127^\circ\text{C}$ by d.s.c. measurement at a heating rate of $10^\circ/\text{min}$).

Chromatographic measurements

These were carried out on an Intersmat IGC 15 apparatus fitted with a catharometer according to the general procedure previously described⁵. The PE sample was deposited from *p*-xylene solution on glass beads (specific surface area, $0.016\text{ m}^2/\text{g}$) treated with HMDS: loading 1% w/w, weight of polymer in the column 0.385 g as checked by calcination.

The retention times were measured within the range $135\text{--}175^\circ\text{C}$. They were a function of the amount of solute injected over the range $0.001\text{--}0.1\ \mu\text{l}$ only for highly polar probes (DMF, DMA, DMSO) and for the lowest temperatures. Linear extrapolations of the experimental data to zero sample size were systematically performed in these cases.

The experimental V_g° values (see below) were compared with the corresponding literature data whenever possible. The values for *n*-decane and *n*-dodecane measured at 145.4 and 153.3°C are systematically lower than those obtained on the same system in an interlaboratory comparison⁶ but the differences 3.5–5% remain reasonable.

Data treatment

The specific retention volumes at infinite dilution, V_g° (cm^3/g), were computed in the usual manner from the retention times t_r of the probes on W g of polymer in the chromatographic columns as follows:

$$V_g^\circ = \frac{t_r F J}{W} \quad (1)$$

where F is the carrier gas flow rate at 0°C and 1 Torr, J is the James–Martin correction factor for gas compressibility.

The activity coefficients at infinite dilution, Ω_1° , based on weight fraction were derived from the corresponding V_g° according to Patterson *et al.*⁷

$$\ln \Omega_1^\circ = \ln \frac{273.2R}{P_1^\circ V_g^\circ M_1} - \frac{P_1^\circ}{RT} (B_{11} - V_1) \quad (2)$$

where subscript 1 refers to solute, M_1 is the molecular weight and P_1° , V_1 and B_{11} are the saturation vapour pressure, the liquid state molar volume and the gas state second virial coefficient at temperature T , respectively. P_1° is calculated from the Antoine equation selecting the corresponding constants from Dreisbach or Boublik compilations^{8,9}. The B_{11} values are estimated from the correlation given by O'Connell and Prausnitz¹⁰.

The partial molar free energies of mixing at infinite dilution, ΔG_1° , are calculated from the activity coefficients according to the equation

$$\Delta G_1^\circ = RT \ln \Omega_1^\circ \quad (3)$$

The temperature dependence of Ω_1° leads to the determination of the partial molar enthalpy of mixing at infinite dilution, ΔH_1° , through the relation:

$$\Delta H_1^\circ = R \partial \ln \Omega_1^\circ / \partial (1/T) \quad (4)$$

Polarity parameters of the probe solutes

The molecular refractions MR_1 (cm^3) of the probe solutes of refractive index n and molar volume V_1 at 25°C were calculated according to the usual Lorenz–Lorentz type relation:

$$MR_1 = V_1(n^2 - 1)/(n^2 + 2) \quad (5)$$

The dipole moments μ (in Cm, $1D = 3.336 \times 10^{-30}$ Cm) were taken from the McClellan compilation¹¹.

The Hildebrand solubility parameters δ_1 (J cm^{-3})^{0.5} were calculated from the corresponding enthalpies of vaporization ΔH_v ,

$$\delta_1 = \left(\frac{\Delta H_v - RT}{V_1} \right)^{0.5} \quad (6)$$

The ΔH_v values at 140°C were in most cases directly found in the literature⁸ or estimated from vapour pressure data.

RESULTS

The values of the partial molar free energy of mixing ΔG_1° at 140°C and of partial molar enthalpy of mixing ΔH_1° calculated between 135 and 175°C are given in Table 1 for all the systems under investigation and for some other ones taken from literature^{12,13}. The molar volume V_1 (140°C) and the polarity parameters (MR_1 and μ_1 at 25°C and δ_1 at 140°C) of the various solutes are quoted in the same table.

ΔG_1° and ΔH_1° are systematically positive and relatively high for the more polar probes. This characteristic feature merely reflects the fact that no specific interaction can occur in the completely apolar PE solvent. Moreover ΔG_1° values are always greater than the ΔH_1° ones. The entropic term $T\Delta S$ is thus negative and opposed to mixing. As expected, the less polar *n*-alkanes from C_6 to C_{12} lead to the lowest ΔH_1° values ($\Delta H_1^\circ < 1\text{ kJ mol}^{-1}$). They decrease with the chain length of the alkane, and the entropic term remains nearly constant, at about -4.5 kJ mol^{-1} in this homologous series. The very weak positive and the strongly negative values of the enthalpic and entropic terms, respectively, suggest that the PE– C_7 to C_{10} systems could show a characteristic LCST of about 140°C , as compared with the experimental LCST of 90°C observed for the PE–*n*-pentane system¹⁴.

DISCUSSION

The partial molar enthalpy of mixing, ΔH_1° , is associated with the formation in the mixture of new (1–2) contacts in place of some original (1–1) and (2–2) ones in the pure components. Thus ΔH_1° is proportional to an interchange energy, ΔW , related to contact energies ϵ_{ij} according to the well known equation:

$$\Delta H_1^\circ \propto \Delta W = 1/2(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}) \quad (7)$$

Besides polymer–solute interactions ΔH_1° also involves solute–solute interactions through the ϵ_{11} term. Probe cohesion is usually measured by its Hildebrand solubility parameter δ , defined as the square root of its cohesive energy density ($\delta_1 \equiv (\Delta E_v/V_1)^{0.5}$).

In the case of the non-polar polyethylene, polymer–

Table 1 Molar volume, polarity parameters of the pure solutes and their partial molar energies and enthalpies of mixing with linear PE

Solute ^a	MR_1	$\mu_1 \times 10^{30}$	V_1	δ_1	$\overline{\Delta H}_1^\infty$	$\overline{\Delta G}_1^\infty$
	(cm ³)	(Cm) 298 K	(cm ³ mol ⁻¹) 413 K	(J cm ⁻³) ^{0.5} 413 K	(kJ mol ⁻¹) 408–448 K	(kJ mol ⁻¹) 413 K
1 n-heptane	34.6	0	174.7	12.1	1.05	5.7
2 n-octane	39.2	0	188.4	12.6	1.02	5.3
3 n-decane	48.5	0	223.2	13.2	0.8	5.13
4 n-dodecane	57.8	0	256.5	13.6	0.6	4.88
5 cyclohexane	27.0	0	127.9	13.5	0.90	4.62
6 carbon tetrachloride	26.4	0	112.5	14.4	1.59	2.4
7 chloroform	21.0	3.4	84.7	15.7	2.7	3.27
8 1,1,2-trichlorethane	25.9	5.2	106.3	16.5	4.14	4.33
9 1,1,1,2-tetrachlorethane	30.6	5.7	119.0	16.7	2.94	3.5
10 1-chlorobutane	25.5	6.3	122.7	14.0	2.8	5.15
11 1-chlorohexane	34.8	6.6	156.9	14.2	2.47	4.69
12 1,5-dichloropentane	35.5	7.8	143.8	16.4	3.91	5.2
13 benzene	26.2	0	105.3	15.1	1.46	4.85
14 toluene	31.1	1.1	122.7	15.2	1.84	4.88
15 chlorobenzene	31.2	5.1	116.0	16.4	2.73	3.86
16 di-n-propylether	31.7	4.4	162.5	13.3	3.41	5.8
17 di-n-propyl thioether	37.8	5.4	162.0	14.3	1.6	4.9
18 butyl acetate	31.1	6.1	153.0	14.3	4.44	6.27
19 ethyl propionate	26.8	5.8	135.0	14.8	5.11	6.4
20 2-butanone	20.7	9.2	109.1	15.1	4.95	6.90
21 2-pentanone	25.2	9.2	126.7	14.7	4.1	6.39
22 cyclohexanone	27.9	10.0	116.9	18.4	7.41	6.73
22 N,N-dimethylformamide	19.9	13.0	87.8	20.1	9.8	9.86
24 N,N-dimethylacetamide	24.3	12.7	105.2	19.6	8.9	9.27
25 dimethyl sulphoxide	20.2	13.0	81.0	22.0	9.55	11.3

* Solutes 6, 13, 21 are from ref. (12) and solutes 1, 11, 12, 16, 17 from ref. (13)

Table 2 Correlation matrix between the partial molar free energy or enthalpy of mixing and the solute polarity parameters

	MR_1	μ_1	μ_1^2
MR_1	1		
μ_1	-0.55	1	
μ_1^2	-0.51		1
$\overline{\Delta G}_1^\infty$	-0.33	0.74	0.87
$\overline{\Delta H}_1^\infty$	-0.61	0.92	0.95

solute interactions are necessarily weak and restricted to repulsive London dispersion forces, dependent on the molecular refraction of the probe MR_1 , (see Experimental section) and to attractive Debye induction forces, dependent on its dipole moment μ_1 . I have thus tentatively analysed the variations of the partial molar free energy and enthalpy of mixing according to two distinct approaches. The first involves correlation analysis of $\overline{\Delta G}_1^\infty$ and $\overline{\Delta H}_1^\infty$ values with MR_1 and μ_1 , chosen as pertinent polarity parameters for quantitative description of polymer-solute interactions. The second involves the classical Hildebrand-Scatchard theoretical framework initially developed for completely apolar systems. It emphasizes the major role of the solute cohesion.

Correlation analysis of the $\overline{\Delta G}_1^\infty$ and $\overline{\Delta H}_1^\infty$ thermodynamic data with probe polarity

The correlation matrix between $\overline{\Delta G}_1^\infty$, $\overline{\Delta H}_1^\infty$, μ_1^2 and MR_1 is given in Table 2. μ_1 and MR_1 are independent

variables and stepwise regression analysis of $\overline{\Delta G}_1^\infty$ and $\overline{\Delta H}_1^\infty$ versus μ_1 and MR_1 shows that the introduction of the molecular refraction MR_1 as a second variable does not lead to any significant improvement of the correlation according to *f* statistics¹⁵. The $\overline{\Delta G}_1^\infty$ and $\overline{\Delta H}_1^\infty$ variations may be thus analysed using the solute dipole moment as the only polarity descriptor, as shown by the following correlations:

$$\overline{\Delta G}_1^\infty (\text{kJ mol}^{-1}) = 4.20 \pm 0.032(\mu_1 \times 10^{30})^2 (\text{Cm})$$

$$R(25) = 0.8667 \quad \bar{\sigma} = 1.03 \quad (8)$$

$$\overline{\Delta H}_1^\infty (\text{kJ mol}^{-1}) = 1.43 \pm 0.048(\mu_1 \times 10^{30})^2 (\text{Cm})$$

$$R(25) = 0.9480 \quad \bar{\sigma} = 0.89 \quad (9)$$

They are statistically significant (see regression coefficient *R* and mean-square standard deviation $\bar{\sigma}$), and both $\overline{\Delta G}_1^\infty$ and $\overline{\Delta H}_1^\infty$ appear as increasing functions of the dipole moment of the probe. The correlation is also better for $\overline{\Delta H}_1^\infty$ than for $\overline{\Delta G}_1^\infty$ variations (Figure 1). This feature may be at least partly ascribed to the relative inaccuracy of the $\overline{\Delta G}_1^\infty$ values which arises both from the experimental measurement and from the data reduction (see Experimental section) and which is further enhanced when dealing with literature data from various sources.

The best correlation, $\overline{\Delta H}_1^\infty$ vs. μ_1^2 , is worthy of further discussion on both statistical and physical grounds. One third of the residuals $|\overline{\Delta H}_1^\infty \text{ calc.} - \overline{\Delta H}_1^\infty \text{ exp.}|$ lie in the range $1,2\sigma$ (Figure 1) and the corresponding solutes do not belong to a definite class but show all types of

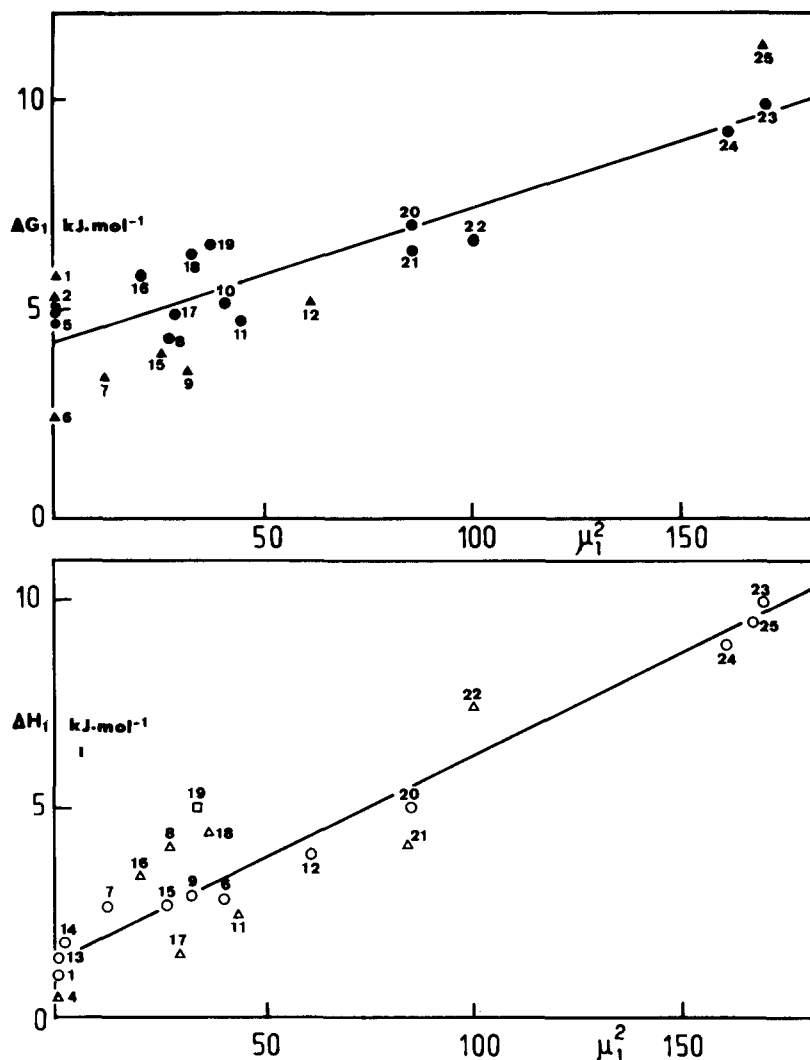


Figure 1 Variations of $\overline{\Delta G}_1^\circ$ and $\overline{\Delta H}_1^\circ$ with the dipole moment of the probes. The numbers refer to the solutes given in Table 1: \circ , residual $< 1\sigma$; \triangle , $1\bar{\sigma} < - < 2\bar{\sigma}$; \square , $> 2\bar{\sigma}$

functionality going from non-polar alkane, to alkylchloride, ester, ketone and finally sulphoxide (solutes 4, 9, 19, 21, 25). Adsorption phenomena may contribute to the apparently overestimated $\overline{\Delta H}_1^\circ$ exp. values for the highly dipolar and self-associated probes such as dimethylformamide, dimethylacetamide or dimethylsulphoxide. However, no definite explanation may be proposed for the apparently underestimated $\overline{\Delta H}_1^\circ$ exp. values observed for monochloroalkanes, for instance.

Solubility in the non-polar polyethylene is to decrease with probe polarity, and the positive contribution of the μ_1^2 term to $\overline{\Delta H}_1^\circ$ is thus physically meaningful. However, it must be emphasized that in this special case the μ_1^2 term cannot be related to weak polymer-solute Debye interactions which should lead to a negative contribution to $\overline{\Delta H}_1^\circ$; the $(\mu_1^2)_1$ term may instead be interpreted as a measure of the probe cohesion. For the series of solutes under investigation which involves mainly polar aprotic species the contribution of dipolar interactions to the total solute cohesion is the major one, so that μ and δ are not independent: $R(25) = 0.79$. Such a specific feature is not observed for broader populations involving all types of solutes, such as that analysed by Chastrette *et al.*¹⁷.

The positive weak constant term of about 1.4 kJ mol^{-1}

may be tentatively ascribed to the contribution of the London dispersion interactions. It is compatible with the $\overline{\Delta H}_1^\circ$ low values observed for n-alkanes, CCl_4 and benzene ($\mu_1 = 0$) when taking into account the experimental accuracy of about 0.5 kJ mol^{-1} . London dispersion interactions are a function of the molecular refraction of the probe, and the lack of any statistically significant MR_1 term in the correlations may be ascribed to the too low $\overline{\Delta H}_1^\circ$ values observed for the completely apolar binary systems and to the by far prevailing contribution of the μ_1^2 term for the others.

Analysis of the $\overline{\Delta G}_1^\circ$ and $\overline{\Delta H}_1^\circ$ thermodynamic data in terms of solubility parameters according to the Hildebrand-Scatchard theory

The theoretical framework developed by Hildebrand¹⁶ for the quantitative analysis of the mutual solubility of low molecular weight species is related to non-polar systems when the lack of any specific interactions between the two compounds lead to positive partial molar free energy and enthalpy of mixing. This approach extended to the infinite dilution conditions of g.l.c. experiments carried out on solvent-polymer systems¹⁸, describes the free energy of mixing, $\overline{\Delta G}_1^\circ$, as a simple function of

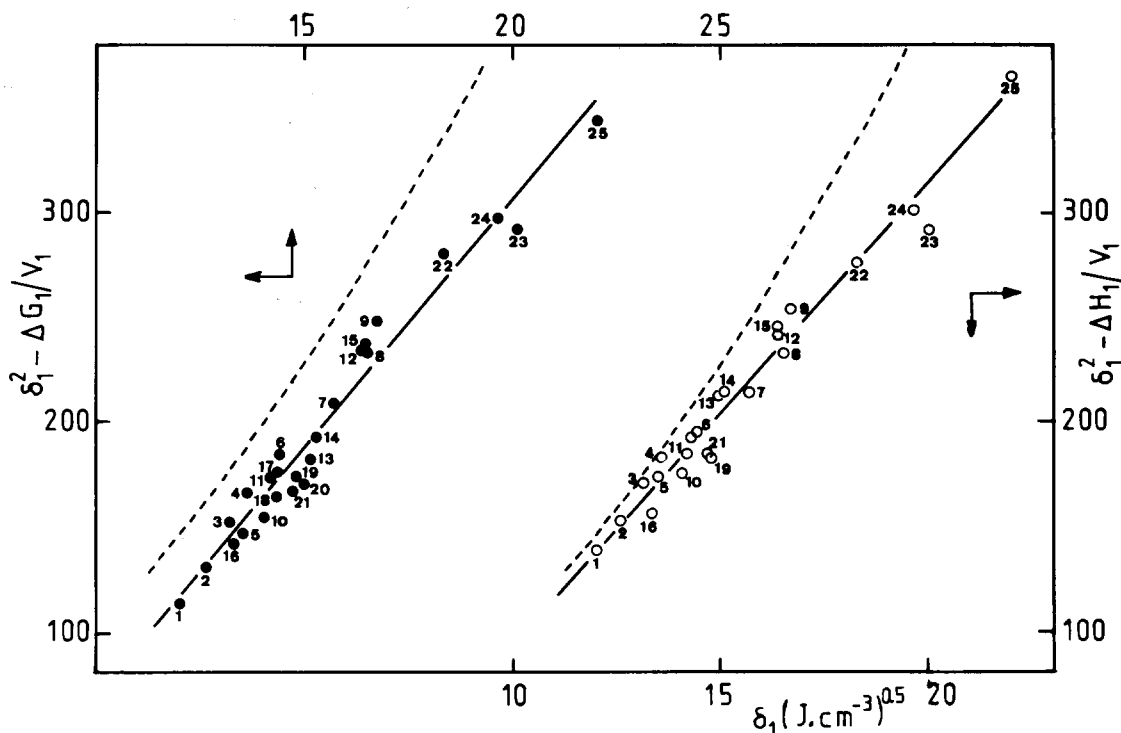


Figure 2 Derivation of the solubility parameter δ_2 of PE at 140°C according to equations (16) and (17). ----, parabola $\delta_1^2/RT=F(\delta_1)$

the solubility parameters of the two components according to:

$$\overline{\Delta G_1^\infty} = V_1(\delta_1 - \delta_2)^2 \quad (10)$$

Assuming no volume change on mixing, the same equation also holds for $\overline{\Delta H_1^\infty}$. Following a treatment first proposed by Watson *et al.*¹⁹, Guillet *et al.*²⁰ have rearranged the previous equation in the following form:

$$\delta_1^2 - (\overline{\Delta G_1^\infty}/V_1) = 2\delta_1\delta_2 - \delta_2^2 = \delta_1^2 - (\overline{\Delta H_1^\infty}/V_1) \quad (11)$$

mixing at constant pressure mixing at constant volume

It allows a straightforward linearization of the experimental data (plot of $\delta_1^2 - (\overline{\Delta G_1^\infty}/V_1)$ versus δ_1 , for instance) and the calculation of the polymer solubility parameter δ_2 . This approach has become popular and widely used in g.l.c. literature. Because the dipole moment and the solubility parameter of the probes are rather strongly interdependent as previously noted, I first tried to see if there were any simple correlations between $\overline{\Delta G_1^\infty}$ or $\overline{\Delta H_1^\infty}$ and δ_1 before testing equation (11). Linear regression analysis lead to the following correlations:

$$\overline{\Delta G_1^\infty} (\text{kJ mol}^{-1}) = -2.89 + 0.55 \delta_1$$

$$R(25) = 0.6614 \quad \bar{\sigma} = 1.55 \quad (12)$$

$$\overline{\Delta H_1^\infty} (\text{kJ mol}^{-1}) = -11.7 + 0.924 \delta_1$$

$$R(25) = 0.8771 \quad \bar{\sigma} = 1.35 \quad (13)$$

$\overline{\Delta G_1^\infty}$ and δ_1 are practically not correlated, but the correlation $\overline{\Delta H_1^\infty} - \delta_1$, although of relative poor quality, is statistically significant. It is, for instance, far better than the rather strong scatter observed by Guillet *et al.*²⁰ for similar correlations related to poly(styrene) or poly(methylmethacrylate) and a series of aliphatic and aromatic hydrocarbons.

Table 3 Calculated values of the δ_2 parameter for linear PE at 140°C (J cm^{-3})^{0.5}

Correlation	$\overline{\Delta H_1^\infty} = 0$	Slope	Intercept
(17) $\overline{\Delta H_1^\infty}/V_1$ vs. δ_1	12.8 ± 1		
(19) $\delta_1^2 - \overline{\Delta H_1^\infty}/V_1$ vs. δ_1		10.8 ± 0.5	11.1 ± 0.5
(18) $\delta_1^2 - \overline{\Delta G_1^\infty}/V_1$ vs. δ_1		11.8 ± 0.5	12.9 ± 0.5

Normalization of the $\overline{\Delta G_1^\infty}$ and $\overline{\Delta H_1^\infty}$ values by the molar volume of the probe V_1 as suggested by the theory, significantly improves the correlation, especially for the $\overline{\Delta G_1^\infty}$ variations:

$$\overline{\Delta G_1^\infty}/V_1 (\text{J cm}^{-3}) = -106 + 9.9 \delta_1$$

$$R(25) = 0.8459 \quad \bar{\sigma} = 15.4 \quad (14)$$

$$\overline{\Delta H_1^\infty}/V_1 (\text{J cm}^{-3}) = -152 + 11.9 \delta_1$$

$$R(25) = 0.9203 \quad \bar{\sigma} = 12.6 \quad (15)$$

Finally the experimental variations of both $\overline{\Delta G_1^\infty}$ and $\overline{\Delta H_1^\infty}$ with probe solubility parameter are in very good agreement with equation (11), as shown in Figure 2.

$$\delta_1^2 - \overline{\Delta G_1^\infty}/V_1 = -168 + 23.7 \delta_1$$

$$R(25) = 0.9807 \quad \bar{\sigma} = 11.7 \quad (16)$$

$$\delta_1^2 - \overline{\Delta H_1^\infty}/V_1 = -122.3 + 21.64 \delta_1$$

$$R(25) = 0.9796 \quad \bar{\sigma} = 11.0 \quad (17)$$

The values of the PE solubility parameter δ_2 at 140°C derived from the only fair correlation 15 and from the better ones 16 and 17 of similar goodness on statistical grounds are given in Table 3. In the latter case, the values derived from the $\overline{\Delta G_1^\infty}$ variations, and more especially that calculated from the intercept, are slightly higher than

the others. This merely reflects that the $\overline{\Delta G_1^\infty - \delta_1}$ equation should include an entropic term, and that the true intercept is $\delta_2^2 - T\Delta S/V_1$ ($\Delta S < 0$) instead of δ_2^2 .

The more reliable δ_2 value is thus $\delta_2 = 11.3 \pm 0.5$ (J cm^{-3})^{0.5}, which is weaker than the δ_1 value of n-decane (model alkane) at the same temperature ($\delta_1 = 13.2$ (J cm^{-3})^{0.5} and that the δ_2 value derived from swelling measurements²¹ at 25°C $\delta_2 = 16.2$ (J cm^{-3})^{0.5}. The difference in the latter case may be ascribed at least partly to temperature effects because δ is a decreasing function of temperature.

As already emphasized²², the very good linearity generally observed in the plot of experimental data according to equation (11) may be somewhat artificial. It arises partly from two contributions: the weakness of the term $\overline{\Delta G_1^\infty}/V_1$ or $\overline{\Delta H_1^\infty}/V_1$ with respect to δ_1^2 , in most cases and the very strong linear correlation between δ_1 and δ_1^2 for solutes covering a δ range between 15 (alkanes) and 25 (DMSO), $R(25) = 0.99$ for our population, for instance. In the system studied here however, for the more polar solutes, the $\overline{\Delta G_1^\infty}/V_1$ and $\overline{\Delta H_1^\infty}/V_1$ terms are no more negligible with respect to δ_1^2 . They raise up to about 20% for esters and ketones, and to about 30% for carboxylic tertiary amides. The deviation of the experimental points from the δ_1^2 vs. δ_1 quasi-linear curve and the good fit observed with equation (11) are thus physically meaningful, and the calculated δ_2 values may be considered as reliable.

CONCLUSION

The thermodynamics of interaction between molten linear PE and volatile solutes are dominated by their molecular cohesion over a very broad range of solute polarity. This feature is characteristic of a non-polar polymer and should be typical of many other polyolefins and probably polydialkylsiloxanes. For binary polar systems however, specific solute-polymer interactions may strongly prevail over probe cohesion contribution and lead to negative partial molar enthalpy of mixing at infinite dilution. I have already shown that for poly(vinylidene fluoride), for instance, the $\overline{\Delta H_1^\infty}$ variations may be quantitatively interpreted in terms of the dipole moment and the hydrogen bond accepting power of the probe²³. In a forthcoming communication, I shall extend this semi-empirical approach to various other polar polymers. Correlation analysis of the $\overline{\Delta H_1^\infty}$ variations with probe polarity through linear multiparametric regression will be shown to be of general value, provided that the independent probe polarity parameters are well

chosen and finely tuned to the polymer structure in order to account for all types of possible interactions in a given system.

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APPENDIX

According to a referee's comment, the concept of the three dimensional solubility parameter as proposed by Hansen²¹ should be of interest in the quantitative analysis of polymer-probe interactions. I prefer to avoid this approach for the following reasons. The individual solubility parameters are better considered as cohesion rather than interaction parameters. The δ_d ($\delta_d \propto n$) arising from dispersion forces and δ_p ($\delta_p \propto \mu$) from the dipolar ones, have no clear advantages over MR and μ for the description of dispersive and dipolar interactions.