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Thermodynamic studies on polyether–solvent systems by gas–liquid chromatography

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The partial molar enthalpies of mixing at infinite dilution $\overline{\Delta H}{}_1^{\infty}$ of a series of 23 solvents (1), covering a fairly broad range of polarity, with liquid poly(ethylene oxide) and poly(tetramethylene oxide) (2) have been measured by gas–liquid chromatography over the range 70–140°C. The variations of $\overline{\Delta H}{}_1^{\infty}$ have been analysed in terms of probe structure through linear multiparametric correlations involving the molar volume V (or molecular refraction MR), the lowest unoccupied molecular orbital (LUMO) energy ϵ_L and the hydrogen-bond donating power α (Taft scale) as probe polarity descriptors. Statistically significant correlations are obtained, emphasizing that an exothermic mixing process arises essentially from negative contributions of the ϵ_L and α terms: the ether function of the chain behaves as an n-donor and as a hydrogen-bond acceptor. The positive contribution of the MR term is a direct measure of the cavitation effects: for the two polyethers, and polystyrene, poly(vinyl acetate) and poly(vinylidene fluoride) previously studied, the corresponding coefficients of the MR term are an increasing linear function of the cohesive energy density of the polymers as measured by the square of their Hildebrand solubility parameters δ^2.

(Keywords: polymer–probe interactions; gas–liquid chromatography; multiparametric correlation analysis)

INTRODUCTION

Gas–liquid chromatography (g.l.c.) is now well established as a reliable method for the study of solute (1)–polymer (2) interactions at infinite dilution of the probe. It allows derivation of accurate values of the partial molar enthalpy of mixing of the low molecular weight probe with the liquid polymer phase, $\overline{\Delta H}{}_1^{\infty}$, as the most relevant thermodynamic parameter of the mixing process[1,2]. The probe solubilization may involve a quite complex process, more especially for polar systems where specific probe–polymer interactions (e.g. hydrogen bonding, electron donor–acceptor interactions) may lead to an exothermic mixing process. A pure theoretical approach to these solvation phenomena is obviously not available at this time, but our previous work[3] on polystyrene, poly(vinyl acetate) and poly(vinylidene fluoride) has shown that rationalization of the $\overline{\Delta H}{}_1^{\infty}$ variations with probe structure in terms of interactions at a molecular level is actually possible through an empirical method based on the 'linear solvation energy relationship' developed by Taft and co-workers[4].

Thus, the present study was performed with three main goals:

1. the g.l.c. measurements of the $\overline{\Delta H}{}_1^{\infty}$ values for two linear polyethers of closely related structure, poly(ethylene oxide) (PEO) and poly(tetramethylene oxide) (PTMO), studied within the temperature range 70–140°C and with a set of 23 solvents covering a fairly broad range of polarity;
2. the interpretation of the $\overline{\Delta H}{}_1^{\infty}$ variations with probe structure within the previously developed framework (linear multiparametric regression analysis) to check its versatility and its reliability;
3. the comparison of bulk polarities of the five polymers of the previous and present studies.

EXPERIMENTAL

Probe molecules and polymeric stationary phases

Alkanes, chloroalkanes and aromatic hydrocarbons of the best 'chromatography' grade were used as received. The other solvents were purified by distillation over convenient drying reagents according to literature procedures.

PTMO is a home-made polymer prepared by cationic polymerization of tetrahydrofuran in bulk at −5°C initiated by trifluoromethanesulfonic anhydride[5]. PEO is a H15000 sample from Hoechst, where hydroxyl end groups were quantitatively methylated as previously described[6]. The specific volumes in the liquid state of the two polymers obey the following relations:

$$\mathrm{PEO}\,v_2(\mathrm{g\,cm^{-3}}) = 0.9217 + 6.9 \times 10^{-4}(t - 70) \qquad 70 < t < 100^{\circ}\mathrm{C} \quad (\text{ref. 7})$$

$$\mathrm{PTMO}\,v_2(\mathrm{g\,cm^{-3}}) = 1.0002 + 7.35 \times 10^{-4}t \qquad (\text{ref. 8})$$

with thermal expansion coefficients α of 0.75×10^{-3} and $0.72 \times 10^{-3}\,\mathrm{K^{-1}}$, respectively.

Chromatographic measurements

Chromatographic measurements were carried out on an Intersmat IGC 15 apparatus fitted with a catharometer. The column oven temperature was controlled

Table 1 Stationary phases and column characteristics

Polymer	$M_w(M_w/M_n)$	T_m (°C)	Coating solvent	Column length (cm)	Loading (%, w/w)[a]	Weight of polymer (g)[b]
PEO	15 000 (1.1)	65	$CHCl_3$	70	9.0	0.680
PTMO	27 600 (1.3)	45	THF	70 140	8.8	0.620 1.276

[a] Inert support: chrom G, AW, DMCS, 60/80

[b] Determined by calcination after a blank correction; in both cases wt/initial calc. wt = 0.85

within ±0.05°C. The flow rate of helium used as carrier gas was measured at the column outlet by a soap-bubble flowmeter. The inlet pressure was monitored by a mercury manometer and the outlet was at atmospheric pressure. The characteristics of the various columns are detailed in *Table 1*. The specific retention volumes at infinite dilution, V_g°, were measured for the various solutes generally within a temperature range of 70–140°C. For both polymers, the V_g° values are independent of the probe size over the range 0.001–0.1 μl and independent of the gas vector flow rate within the range of 8–20 ml min^{-1}. The measurements were thus systematically performed at a 10 ml min^{-1} flow rate.

Data treatment

The specific retention volumes at infinite dilution, V_g° (cm^3 g^{-1}, 0°C, 760 mmHg), were computed in the usual manner from the retention times t_r of the probes on W grams of polymer in the chromatographic columns:

$$V_g^\circ = \frac{F}{W} t_r \times \frac{273.2}{T_a} \times \frac{760}{P_a} \times \frac{P_a - P_w}{P_a} \times J \qquad (1)$$

where F is the carrier gas flow rate at temperature T_a and pressure P_a, $(P_a - P_w)/P_a$ is the correction of the flow rate for the water vapour pressure, and J is the James–Martin correction factor for gas compressibility.

At temperatures above the melting point of the polymer, the magnitude of V_g° is a measure of the solubility of the probe in the liquid polymer. The partial molar heat of solution ΔH_s is given by the temperature dependence of V_g°:

$$\overline{\Delta H}_s = -R \partial \ln V_g^\circ / \partial(1/T) \qquad (2)$$

where R is the gas constant.

The activity coefficient at infinite dilution, Ω_1^∞, based on weight fraction, was derived from the corresponding V_g° according to Patterson *et al.*[9]:

$$\ln \Omega_1^\infty = \ln \frac{273.2R}{P_1^\circ V_g^\circ M_1} - \frac{P_1^\circ}{RT}(B_{11} - V_1) \qquad (3)$$

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[10–12] and from compilations by Boublik *et al.*[13]. The B_{11} values are estimated from the correlation given by Reid *et al.*[14].

The temperature dependence of Ω_1^∞ leads to the determination of the partial molar enthalpy of mixing at infinite dilution, $\overline{\Delta H}_1^\infty$, through the relation:

$$\overline{\Delta H}_1^\infty = R \partial \ln \Omega_1^\infty / \partial(1/T) \qquad (4)$$

ΔH_S and $\overline{\Delta H}_1^\infty$ are correlated through the relation:

$$-\Delta H_S = \Delta H_V - \overline{\Delta H}_1^\infty \qquad (5)$$

where ΔH_V is the molar enthalpy of vaporization of the probe. It should be emphasized that the inaccuracy on the polymer weight, which has been recognized as one of the major sources of error in g.l.c. experiments[15], has no influence on the $\overline{\Delta H}_1^\infty$ values calculated from equation (4).

The activity coefficient of the solute probe at infinite dilution, Ω_1^∞, is correlated with the interaction parameter based on segment fraction χ_{12}^*, according to ref. 9 through the equation:

$$\ln \Omega_1^\infty = 1 + \chi_{12}^* + \ln v_1^*/v_2^* \qquad (6)$$

where v^* are the specific volumes at 0 K (core volumes). χ_{12}^* is generally assumed to result from two additive contributions related to interactional or contact energy between polymer segments and the solute, and to free volume, respectively. The contact term is given by[16]:

$$X_{12} = RT(\tilde{v}_2/v_1^*)\chi^*$$

$$-P_1^*\tilde{v}_2\{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}_2^{1/3} - 1)] + \tilde{v}_1^{-1} - \tilde{v}_2^{-1}\} \qquad (7)$$

where the asterisks represent reduction parameters, and $\tilde{v}$ and $\tilde{T}$ are reduced quantities. The theoretical model of Flory allows $\tilde{v}$ and $\tilde{T}$ to be calculated from the experimental value of the thermal expansion coefficient α according to:

$$\tilde{v}^{1/3} - 1 = \alpha T / 3(1 + \alpha T) \qquad (8)$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \qquad (9)$$

A good approximation of P^*, as proposed by Biros *et al.*[17], involves the solubility parameter δ according to:

$$P^* = (\delta \tilde{v})^2 \qquad (10)$$

Polarity parameters of the probe solutes

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

$$MR = V_1(n^2 - 1)/(n^2 + 1) \qquad (11)$$

The dipole moments, μ (in C m, 1 D = 3.336×10^{-30} C m), were taken from the McClellan compilation[18].

The hydrogen-bond donating power of the solutes was measured by the solvatochromic empirical parameter α as defined by Taft and co-workers: its value was taken from their recent compilation[19].

The highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) energies ϵ_H and ϵ_L (in eV) of the solutes were taken from the literature[3,20]. Even though the extended Huckel theory (EHT) method does not give accurate absolute values of the energy levels, their trends are well ascertained and these primary values may be safely used for comparative studies.

RESULTS AND DISCUSSION

Heats of solution at infinite dilution ΔH_S

The ΔH_S values, derived according to equation (2) and given in *Table 2*, are only slightly higher or lower than the heats of vaporization of the various probe solutes which afford the major contribution to ΔH_S, depending on whether the partial molar heats of mixing, $\overline{\Delta H_1^{\infty}}$, are positive or negative. However, some general trends may be ascertained according to probe nature, as shown below.

For alkanes:

$$-\Delta H_S\text{PEO} < -\Delta H_S\text{PTMO} < \Delta H_V \rightarrow \overline{\Delta H_1^{\infty}}\text{PEO} > \overline{\Delta H_1^{\infty}}\text{PTMO} > 0$$

For esters and ketones:

$$-\Delta H_S\text{PEO} \approx -\Delta H_S\text{PTMO} > \Delta H_V \rightarrow \overline{\Delta H_1^{\infty}} < 0$$

For aromatic species:

$$-\Delta H_S\text{PEO} \approx -\Delta H_S\text{PTMO} > \Delta H_V \rightarrow \overline{\Delta H_1^{\infty}} < 0$$

For chloroalkanes with weak hydrogen-bond donating power such as CH_2Cl_2 and $CHCl_3$:

$$-\Delta H_S\text{PEO} > -\Delta H_S\text{PTMO} > \Delta H_V \rightarrow \overline{\Delta H_1^{\infty}}\text{PEO} < \overline{\Delta H_1^{\infty}}\text{PTMO} < 0$$

Partial molar enthalpies of mixing at infinite dilution $\overline{\Delta H_1^{\infty}}$

For most systems under study, the thermal variations of the activity coefficients, Ω_1^{∞}, obey equation (4): a fairly good linearity of ln Ω_1^{∞} *versus* $1/T$ is actually observed over the whole temperature range (70–140°C), with typical regression coefficients higher than 0.95 for seven to ten data points. The $\overline{\Delta H_1^{\infty}}$ values thus derived, the calculated interaction parameters χ_{12} at 100°C, and the contact energy parameter X_{12} are given in *Table 3*.

Only in the systems PTMO/acetone or PTMO/ethyl acetate do the variations of ln Ω_1^{∞} *versus* $1/T$ go through a minimum at about 100–120°C: $\overline{\Delta H_1^{\infty}}$ values were thus estimated from the experimental data restricted to the lower temperature range. This behaviour is consistent with the increasing free-volume contribution that is predominant above the boiling point of the solute. The systems should show a typical lower critical solution temperature (*LCST*) behaviour, as also suggested by the maximum observed in the thermal variations of the intrinsic viscosity of PTMO in ethyl acetate solution[21].

Some general trends clearly appear from the results given in *Table 3*. First, as expected, the apolar alkanes, which are non-solvents of both PEO and PTMO, lead to strongly positive $\overline{\Delta H_1^{\infty}}$ and X_{12} values and to χ_{12} values higher than 0.5. Secondly, chlorinated hydrocarbons and, to a lesser extent, aromatic hydrocarbons generally lead to strongly negative $\overline{\Delta H_1^{\infty}}$, χ_{12} and X_{12} values, mainly as a result of strong polymer–solute specific interactions. Donor–acceptor interactions probably occur between the polyether chains and the alkylchloride or the aromatic probes. The ether units behave as n-donors at the oxygen site, alkylchlorides as σ^* acceptors

Table 2 Constants of linear plots of ln V_g° *versus* $1/T$

	PTMO			PEO		
Solute	$-A^a$	$-\Delta H_S/R$ $\times 10^{-3}$	t (°C)	$-A^a$	$-\Delta H_S/R$ $\times 10^{-3}$	t (°C)
1 n-Heptane	6.1850	3.5725	90–120	6.2539	3.2014	65–85
2 n-Decane	7.4390	4.7852	120–135	7.1074	4.1769	75–140
3 Cyclohexane	5.3682	3.2889	90–130			
4 Dichloromethane	6.0630	3.5193	80–120	6.9673	4.1867	70–140
5 Chloroform	6.6711	4.0243	90–130	7.6944	4.3809	70–140
6 Carbon tetrachloride	6.0248	3.6750	80–120	5.9399	3.3874	70–140
7 1,2-Dichloroethane	6.3983	3.9676	95–130	6.9665	4.1860	70–140
8 1-Chlorohexane	7.5498	4.7191	95–130	6.6680	4.1468	100–140
9 1,5-Dichloropentane	7.6775	5.4188	130–160	7.8384	5.4136	130–160
10 Acetone	6.0436	3.3290	80–130	6.0094	3.4012	70–140
11 2-Butanone	6.6897	3.8188	90–130	6.6460	3.8109	70–140
12 Ethyl acetate	6.4220	3.6789	95–130	6.9849	3.8169	90–120
13 Butyl acetate	7.7594	4.6855	105–130	7.4096	4.4321	70–140
14 Tetrahydrofuran	5.7117	3.4771	90–120	6.3335	3.6121	70–140
15 1,4-Dioxane	6.4537	4.0547	95–130	6.8971	4.2189	70–100
16 di-n-Propyl ether	5.1906	3.1948	140–165	5.9235	3.2056	80–140
17 di-n-Propyl thioether	6.7208	4.4634	140–165	6.8192	4.2711	100–140
18 Acetonitrile	5.9001	3.4701	80–120	7.1312	4.1651	70–130
19 Benzene	6.2800	3.8557	90–130	6.6519	3.8620	70–120
20 Toluene	6.6280	4.2494	90–130	7.1750	4.2691	70–120
21 Ethylbenzene	7.4521	4.7759	90–120	7.2179	4.4704	80–140
22 Chlorobenzene	7.2058	4.7640	100–120			
23 Pyridine	7.2398	4.5659	100–120	7.4407	4.6731	105–135

[a] Intercept at the origin of the linear variation of ln V_g° *versus* $1/T$

negative and fairly similar values for polyethers, irrespective of their characteristic ratio r. Finally, for $CHCl_3$, $\overline{\Delta H_1^\infty}$ decreases sharply by about 8 kJ mol^{-1} when going from PE to DOE ($r = 0.06$) and the strongly negative $\overline{\Delta H_1^\infty}$ values are a quasi-linear, slightly decreasing function of r.

Hydrogen bonding thus appears much more efficient and more sensitive to the ether function concentration than the previous donor–acceptor interactions leading to an exothermic solubilization process. However, quantitative discussion of these variations only in terms of solvent–polymer specific interactions is not possible, since the overall $\overline{\Delta H_1^\infty}$ value involves a major contribution of a cavitation term, as will be discussed further.

Correlation analysis of the $\overline{\Delta H_1^\infty}$ *variations with probe polarity*

The general framework of the analysis of the $\overline{\Delta H_1^\infty}$ variations in terms of specific and non-specific solute–solvent interactions through correlation analysis is identical to that successfully developed in our previous study[3]. The $\overline{\Delta H_1^\infty}$ variations may be tentatively quantified through a linear multiparametric equation, where the successive terms are related to all the various types of polymer–probe interactions assumed to be independent and additive:

$$\overline{\Delta H_1^\infty} = \Sigma_i \, d_i D_i$$

where D_i is a descriptor of probe polarity related to only one well defined type i of solute–solvent interaction, and d_i is a parameter characteristic of the liquid polymer phase.

The derivation of a correlation of this type from the experimental data requires the preliminary identification of the various types of interactions i and the best choice of independent and known polarity descriptors D_i for all the solvents under study.

The molecular refraction MR and the dipole moment μ of the probes may be considered as good descriptors for the non-specific Van der Waals interactions[24]. However, the linear correlation which generally holds between MR and the molar volume V is especially strong for the solvent set under study R (23 solvents) $= 0.94$. This unavoidable ambiguity in the true physical meaning of the MR term, already noticed in the development of biochemical quantitative structure–activity relationships[25] and in our previous work[3], will be discussed further.

On the other hand, the ether function essentially behaves as a hydrogen-bond acceptor and an electronic n-donor (essentially towards σ acceptors as alkylchlorides and π acceptors as aromatic compounds). Conversely, the most adjusted probe polarity descriptors are thus the hydrogen-bond donating power α of the solvatochromic Taft scale and the LUMO energy ϵ_L, respectively. This choice from among a number of polarity scales has already been justified[3].

The correlation matrices between the probe polarity descriptors and the experimental $\overline{\Delta H_1^\infty}$ values for the two polyether systems are given in *Table 4*. The selected descriptors MR (or V), ϵ_L and α are independent, and regression analysis leads to the following correlations:

$$\text{PEO}\begin{cases} \overline{\Delta H_1^\infty}(\text{kJ mol}^{-1}) = -1.58 + 0.22MR(\text{ml}) + 0.56\epsilon_L - 7.36\alpha \\ \qquad R(23) = 0.9270 \qquad \sigma = 1.62\,\text{kJ mol}^{-1} \\ \overline{\Delta H_1^\infty}(\text{kJ mol}^{-1}) = -3.80 + 6.3 \times 10^{-2} V_1(\text{ml}) + 0.45\epsilon_L - 7.16\alpha \\ \qquad R(23) = 0.9573 \qquad \sigma = 1.25\,\text{kJ mol}^{-1} \end{cases}$$

$$\text{PTMO}\begin{cases} \overline{\Delta H_1^\infty}(\text{kJ mol}^{-1}) = 1.69 + 2.0 \times 10^{-2} MR(\text{ml}) + 0.33\epsilon_L - 9.49\alpha \\ \qquad R(23) = 0.9250 \qquad \sigma = 0.87\,\text{kJ mol}^{-1} \\ \overline{\Delta H_1^\infty}(\text{kJ mol}^{-1}) = 1.59 + 6 \times 10^{-3} V_1(\text{ml}) + 0.33\epsilon_L - 8.19\alpha \\ \qquad R(23) = 0.9025 \qquad \sigma = 0.96\,\text{kJ mol}^{-1} \end{cases}$$

The normalized coefficients, calculated using centred variables to take into account their different variation ranges[26], directly reflect the sensitivity of the $\overline{\Delta H_1^\infty}$ thermodynamic parameter to the various types of interaction. The comparison of their respective contributions for the solvent set under study is given in *Table 5*.

These linear correlations, although rather poor (see the multiple regression coefficient R and the mean-square standard deviation σ), are statistically significant: four to seven among 23 solvents under study lead to residuals $|\overline{\Delta H_1^\infty}\ \text{calc} - \overline{\Delta H_1^\infty}\ \text{expt}|$ between one and two σ, and only two systems (acetonitrile/PEO and acetonitrile/PTMO) lead to a residual higher than two σ; moreover, the residuals are randomly distributed according to the run test[27]. These correlations may be critically discussed from a number of viewpoints, as follows.

As already noticed, the quasi-colinearity of MR and V does not allow a definite choice between these two descriptors on purely statistical grounds: correlation is slightly better with V for PEO, but not for PTMO. Dispersion interactions should increase the probe solubility and thus lead to a negative contribution of the MR term to the $\overline{\Delta H_1^\infty}$ value: this is actually not observed. On the other hand, a true physical meaning may be ascribed without any ambiguity to the positive contribution of the V term related to cavitation effects: the bulkier the probe, the higher the energy necessary to create a hole in the liquid polymer phase for its accommodation and the higher the endoergic contribution of the V term to $\overline{\Delta H_1^\infty}$.

According to F statistics[28], the introduction of the dipole moment μ of the probe as a complementary term does not allow any significant improvement of the

Table 4 Correlation matrix between $\overline{\Delta H_1^\infty}$ values and the basic physicochemical variables used for the two systems

	V_1 (cm^3 mol^{-1})	MR (cm^3 mol^{-1})	ϵ_L (eV)	μ (C m)	α
MR	0.94				
ϵ_L	0.44	0.30			
μ		−0.51	−0.45		
α	−0.47	−0.49	−0.29		
PEO $\overline{\Delta H_1^\infty}$	0.85	0.73	0.74	−0.48	−0.59
PTMO $\overline{\Delta H_1^\infty}$	0.57	0.41	0.77	0.05	−0.66

Table 5 Contribution (%) of the variables to the $\overline{\Delta H_1^\infty}$ for the set of 23 solvents under study

	V	MR	ϵ_L	α
PEO		39	44	17
	47		36	17
PTMO		6	52	42
	9		52	39

correlations, even if the regression coefficient between $\overline{\Delta H_1^\infty}$ and μ is not negligible in the case of the more polar PEO (see *Table 4*). This feature may reflect the relatively low local dipole moment of the ether function in the liquid polymeric phase, $\mu < 2D$.

The negative contributions of the ϵ_L (ϵ_L is negative) and α terms to $\overline{\Delta H_1^\infty}$ confirm that specific extended Huckel theory interactions and hydrogen bonding are the major driving forces for probe solubilization in the liquid polyethers. The last contribution, identified through only five weak C–H donor solutes, should be quantified more accurately on a higher number of strongly protic probes such as alcohols, in spite of the potential problems arising from their self-association[22].

Comparison of the enthalpic $\overline{\Delta H_1^\infty}$ correlations for various polymeric systems

For a given system, the coefficients of various probe polarity descriptors are obviously characteristic of the liquid polymer under study: they may be considered as its corresponding polarity descriptors with respect to each type of polymer–solvent interaction identified in the correlation. The term by term comparison of the $\overline{\Delta H_1^\infty}$ correlations for different polymers should allow a quantitative comparison of the polymer polarities.

Analysis of the present results and those of our previous studies on poly(vinylidene fluoride) (PVF_2), poly(vinyl acetate) (PVAC) and polystyrene (PS) along these lines points out some interesting features, as discussed below.

The coefficient of the V (or MR) term should reflect the ability of the liquid polymeric phase to allow the formation of a cavity to accommodate the solute. It actually has the dimensions of a cohesion term ($J\,cm^{-3}$) and it is fairly linear with the square of the Hildebrand solubility parameter, δ^2, of the polymers taken from the literature[8,22,23,29–31]: $MR = 1.08\,\delta^2 - 300$, $R(6) = 0.9945$ (*Figure 2*). This typical feature is quite gratifying and consistent with the fact that δ^2 is well established as a measure of the polymer cohesion. The increasing order:

$$\mathrm{PE} < \mathrm{PTMO} < \mathrm{PS} < \mathrm{PVAC} \leq \mathrm{PEO} < \mathrm{PVF_2}$$

may appear fairly consistent with the density and the intrinsic polarity of the polar bonds in the chain.

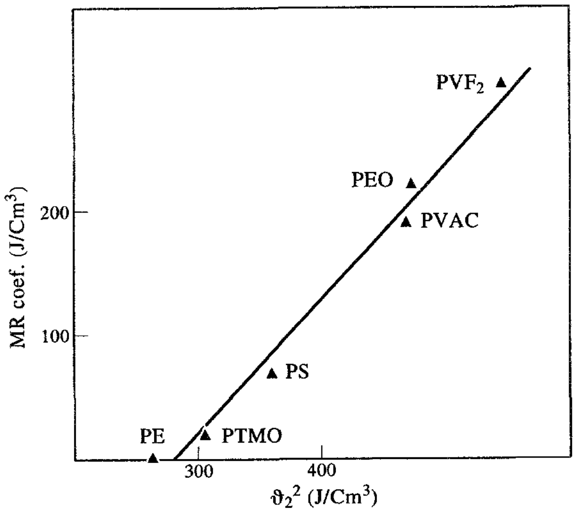

Figure 2 Variation of the coefficient of the MR term in the multiparametric equation with the square of the Hildebrand solubility parameter δ^2 for various polymers

The coefficient of the ϵ_L term should reflect the electron-donor power of the polymer towards acceptor probes according to an increasing order:

$$\mathrm{PTMO}(0.33) < \mathrm{PS}(0.35) < \mathrm{PEO}(0.56) < \mathrm{PVAC}(0.62)$$

It is difficult to discuss the position of the π aromatic donor with respect to the other three n-donors. However the minimum value observed for PTMO may correspond to the lowest density in donor sites in its chain.

Finally, the coefficients of the α term should reflect the hydrogen-bond accepting power of the polymers: they are fairly similar for PTMO and PEO, as expected, because of identical polyether structure of these two homologous chains.

Polymer–polymer miscibility and enthalpic correlations

Negative $\overline{\Delta H_1^\infty}$ values reflect strongly specific interactions between the solvent 1 and the polymer 2, and suggest potential miscibility between the corresponding polymer 1 (carrying repeating units of the same chemical structure as solvent 1) and polymer 2. The previous enthalpic correlations may thus appear of definite interest as a predictive or interpretative tool in the important field of polymer blends. This oversimplified approach has already proved to be quite successful in the search for new miscible polymer pairs, for example, tertiary amide polymers with PVF_2[32,33]. For the polyether chains, the experimental data of *Table 3* may suggest the following comments.

(1) The partial miscibility between PEO and three ester-bearing polymers – poly(methyl acrylate), poly(methyl methacrylate) and PVAC[34,35] – may be directly correlated with the slightly negative value, $\overline{\Delta H_1^\infty} = -0.92\,kJ\,mol^{-1}$, measured for the PEO/ethyl acetate system.

(2) Considering aromatic structures, potential miscibility between PEO or PTMO and PS or poly(vinyl pyridine)s, suggested by the corresponding $\overline{\Delta H_1^\infty}$ values, is not actually observed, while partial miscibility has been claimed for the PEO–poly(β-vinylnaphthalene) pair[36]. It may be recalled that PS and, even more, poly(2-chlorostyrene) are miscible with poly(methyl vinyl ether) which carries the ether function as lateral group[37].

(3) The strongest negative $\overline{\Delta H_1^\infty}$ values measured for the weak hydrogen-bond donors, such as chlorinated hydrocarbons (CH_2Cl_2, $CHCl_3$), may be considered a priori as a strong argument in favour of potential miscibility of the corresponding polymer pairs. To the best of our knowledge, no literature data are available for PEO or PTMO and polymers bearing $CHCl_2$ functional groups.

Because of the unavoidable crudeness of the oversimplification involved in modelling the polymer 1–polymer 2 system by the solvent 1–polymer 2 system, the enthalpic correlations must be considered only as a guide in the field of polymer–polymer miscibility. They are, however, as valuable as the most popular approach of the Hildebrand solubility parameter, which is precisely restricted to non-polar and weakly interacting systems (mixing enthalpy $\Delta \overline{H}_1^\infty \geq 0$).

CONCLUSION

In spite of the lack of sound theoretical grounds, correlation analysis definitely appears to be the most efficient and reliable semi-empirical approach to analysing the thermodynamics of mixing of volatile probes with liquid polymers in terms of non-specific and specific interactions at a molecular level. The enthalpic correlations allow the major trends to be identified from experimental data which cannot be easily rationalized in any other way, and they lead to better insight in important research fields of both technological and basic interest, such as polymer blends and polarity of bulk polymers.

For the mixing process between any solvent 1 and polymer 2, the ultimate goal remains the development of general linear multiparametric correlation, which should be symmetrical in solvent and polymer properties and highly significant on both statistical and physical grounds:

$$P = P_0 + A\delta_2^2 V_1 + Bd_1 d_2$$

where P is a thermodynamic function of the mixing process, $A\delta_2^2 V_1$ is the endoergic cavity term, and Bd_1d_2 is the sum of all the exoergic interaction terms (d_1 and d_2 are the complementary polarity descriptors).

In spite of the inherent difficulty in identifying all the types of interactions and in choosing the most relevant polarity descriptors from a host of partly interconnected polarity scales, our results, and recent literature data obtained within a similar framework[38], clearly show that this ambitious goal remains reasonable.

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