Gas-Liquid Chromatography Study of Polar Polymer-Solvent Systems. Correlation Analysis of the Partial Molar Enthalpy of Mixing with Solvent Polarity

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ABSTRACT: The partial molar enthalpies of mixing at infinite dilution, $\overline{\Delta H_1}^\infty$, of a series of aprotic solvents covering a broad range of polarity from alkanes to hexamethylphosphoric triamide with liquid poly(vinylidene fluoride) (PVF_2, 160-210 °C), poly(vinyl acetate) (PVAC, 110-150 °C), and polystyrene (PS, 150-190 °C) have been measured by gas-liquid chromatography. The variations of $\overline{\Delta H_1}^\infty$ have been tentatively analyzed in terms of probe structure through linear multiparametric correlations involving the molecular refraction, MR, the dipole moment, μ, the hydrogen bond accepting power, β (Taft scale), and the HOMO and LUMO energies, ϵ_H and ϵ_L, as probe polarity descriptors: $\overline{\Delta H_1}^\infty = r\text{MR} + m\mu + b\beta + ...$. For the three polymers, statistically signifiant correlations are obtained, emphasizing the positive contribution of the MR term (London dispersive forces and probe volume) to $\overline{\Delta H_1}^\infty$. An exothermic mixing process arises essentially from negative contribution of the β term for PVF_2 (C-H hydrogen bond donor) and of the ϵ_L term for PVAC (n-donor character of the ester lateral group) and for PS (π-donor properties of the aromatic ring).

Introduction

The partial molar enthalpy of mixing at infinite dilution of a solvent 1 with a polymer 2, $\overline{\Delta H_1}^\infty$, is a most relevant thermodynamic parameter for the description of the solubilization process of low molecular weight species in liquid polymeric phases. It may be readily derived from gas-liquid chromatography (GLC), which is now well established as a reliable method for the study of solute-polymer interactions.[1,2] For a given polymer, the quantitative analysis of the $\overline{\Delta H_1}^\infty$ variations with solute structure at a molecular level still remains an outstanding challenge. For nonpolar or weakly polar systems where intermolecular interactions are restricted to van der Waals ones, the thermodynamics of the mixing process may be interpreted more or less successfully within the framework of "physical" approaches emphasizing, for instance, the influence of the free volume of the probe as measured by its thermal expansion coefficient[3] or of its cohesion as measured by its Hildebrand solubility parameter.[4] For more polar systems, however, specific probe-polymer interactions (hydrogen bonding...) may likely contribute significantly to lower the enthalpy of mixing and to lead possibly to an exothermic mixing process. In this case, the lack of any simple and reliable theory for quantitative description of this type of interaction has not allowed until now a rationalization of the experimental data in a self-consistent way.

The present study was undertaken with two main goals:

(1) the measurement of a large series of $\overline{\Delta H_1}^\infty$ values by GLC for three complementary systems involving poly(vinylidene fluoride) (PVF_2), poly(vinyl acetate) (PVAC), and polystyrene (PS) as polymers and a number of solvents (more than 20) covering a broad range of polarity: both nonspecific and specific interactions are likely to occur simultaneously in these systems.

(2) the development of an empirical approach of the analysis of the $\overline{\Delta H_1}^\infty$ variations with probe structure in terms of molecular interactions for every polymer using the correlation analysis that we already used successfully in a previous study of PVF_2.[5]

It was of definite interest to check the reliability of such an approach by using a significantly broader set of solvents for the same PVF_2 and by checking its generalization to other polymers.

Experimental Section

Probe Molecules and Polymeric Stationary Phases. The 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.[6]

PVF_2, a Kynar 461 sample supplied by Penwalt Corp., was purified by precipitation into water from its dimethylformamide solution and vacuum dried. A linear poly(vinyl acetate) sample was prepared by exhaustive acetylation of poly(vinyl alcohol) from Kurashiki (80 °C, pyridine solution, $[AC_2O]/[OH] = 3$). The polystyrene sample was obtained by anionic polymerization. For all the polymers under investigation, the weight average molecular weights, $\bar{M}_w$ (light scattering), the polydispersity index $\bar{M}_w/\bar{M}_n$ (size-exclusion chromatography), and the glass and possible melting temperature, T_g and T_m (differential scanning calorimetry measurements at a heating rate of 10 °/min) are given in Table I.

Chromatographic measurements were carried out on an Intersmat IGC 15 apparatus fitted with a catharometer. The column oven temperature was controlled 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 pressure was the atmospheric pressure. The characteristics of the various columns are detailed in Table I. The specific retention volumes at infinite dilution, $V_g°$, were measured for a series of aprotic solutes of widely different polarity within a temperature range depending on the polymer: 160-210 °C for PVF_2, 150-190 °C for PS, and 110-150 °C for PVAC. For most of the solutes and each polymer, the $V_g°$ values are independent of the sample size over the range 0.001-0.1 μL. However, for the systems involving chromosorb as inert support and strongly dipolar probes such as tertiary amides, the retention times are a linear decreasing function of the injected amount and need to be extrapolated to zero sample size.

Finally, the $V_g°$ values are independent of the gas vector flow rate within the range of 8-20 mL·min^{-1}, and the measurements were thus systematically performed at a 10 mL·min^{-1} flow rate.

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Table I
Stationary Phases and Column Characteristics

polym	$\bar{M}_w$ $\bar{M}_w/\bar{M}_n$	T_g, °C	coating solvent	column length, cm	inert support	loading, % (w/w)	wt of polym, g
PVF_2	275 000	−45	DMF	120	chrom G, AW, DMCS, 60/80	5.2	0.568
	2.1	T_m = 160.5		120	glass beads, HMDS, 0.016 $m^2 \cdot g^{-1}$	1.3	0.170
PVAC	192 000	32.0	acetone	50	chrom G, AW, DMCS, 60/80	8.5	0.411
	1.7			140		8.5	1.603
PS	69 000	95.3	benzene	70	chrom G, AW, DMCS, 60/80	16.6	0.331
	1.1						

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 grams of polymer in the chromatographic columns

$$V_g° = t_r FJ/W \tag{1}$$

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

At temperatures above T_m or high enough above T_g, the magnitude of $V_g°$ is a measure of the solubility of the probe in the liquid polymer.

The activity coefficient at infinite dilution, Ω_1^∞, based on weight fraction, was derived from the corresponding $V_g°$ according to Patterson et al.[7]

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

where subscript 1 refers to solute, M_1 is the molecular weight, and $P_1°$, V_1, and B_{11} are the saturation vapor 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,[8] from compilations by Boublik, Fried, and Hála,[9] or directly from the literature.[10,11] The B_{11} values are estimated from the correlation given by Reid, Prausnitz, and Sherwood.[12]

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

$$\overline{\Delta H}_1^\infty = R\, \partial \ln \Omega_1^\infty / \partial(1/T) \tag{3}$$

Polarity Parameters of the Probe Solutes. The molecular refractions MR (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:

$$MR = V_1(n^2 - 1)/(n^2 + 2) \tag{4}$$

The dipole moments, μ (in Cm, 1 D = 3.336×10^{-30} Cm) were taken from the McClellan compilation[13] or directly from original literature.[14]

The hydrogen bond donating and accepting powers of the solutes were measured by the solvatochromic empirical parameters α and β as defined by Taft et al.:[15] their values were taken from their recent compilation.[16] For most solvents not yet studied, a primary β value was estimated from the solvatochromic studies of p-nitroaniline and its N,N-diethyl derivative used as reporter probes.[17] As recently recommended by Taft et al.,[16] the β values of the aromatic solutes were taken as a constant equal to 0.12. Our experimental values are 0.01 for 1-chlorohexane and 0.08 for 1,2-dichloroethane or 1,5-dichloropentane: these values were systematically adopted for monochloro- and polychloroalkanes, respectively, instead of the single value of 0.1 proposed by Taft et al.[16]

The HOMO and LUMO energies ϵ_H and ϵ_L (in electronvolts) of the solutes were taken from literature[18] or calculated according to the same EHT method for the solutes not quoted in the previous report.[17] Even though the 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.

Comparison of the Experimental Results with the Corresponding GLC Literature Data. Selected literature data were also taken into account in order to provide a most complete set of experimental results and to check our measurements for some common probes.

For PVF_2, Dipaola–Baranyi $V_g°$ values obtained at 200 °C[19] are only about 3% lower for apolar probes (tetradecane, butylbenzene) and about 6% higher for the dipolar ones (dimethylformamide, cyclohexanone, acetophenone): in the latter case this weak increase may arise from the difference in the inert support used, chromosorb versus glass beads in our measurements.

For PVAC studied at 125 °C, our $V_g°$ values related to n-heptane, 1,2-dichloroethane, toluene, and butanone, for instance, are in good agreement with literature data,[20–22] the difference always being lower than 5%.

For PS, comparison of the calculated Ω_1^∞ values for n-heptane, n-decane, cyclohexane, and benzene studied at 180 ± 5 °C may be performed with a series of literature data.[4,23–25] Our results are in good agreement with those of Guillet and Iwai (difference lower than 5%) while Prausnitz's and Cantow's values are significantly higher and lower, respectively (differences up to 20%). The differences observed with Prausnitz's values may probably arise from an overestimation of the polymer weight in the column (not checked by calcination or extraction), which leads to underestimated $V_g°$ values. We have however no explanation of the discrepancy with Cantow's results (possible variation of the $P_1°$ and B_{11} values involved in the data reduction). It may be emphasized that the inaccuracy on the polymer weight, which has been recognized as one of the major sources of error in GLC experiments,[26] has no influence on the calculated $\overline{\Delta H}_1^\infty$ values.

Experimental Results and Discussion

Partial Molar Enthalpies of Mixing at Infinite Dilution $\overline{\Delta H}_1^\infty$. For the three polymers under study and for most of the probes, the variations of ln Ω_1^∞ versus T^{-1} are linear over the whole temperature range investigated, showing that $\overline{\Delta H}_1^\infty$ from eq 3 is constant. The average absolute error on the $\overline{\Delta H}_1^\infty$ determined from 6 to 10 measurements at different temperatures may be estimated to about ±0.4 $kJ \cdot mol^{-1}$. As expected, for polymer–nonsolvent systems (alkanes with the three polymers for instance), the $\overline{\Delta H}_1^\infty$ values are strongly positive, while they become negative in the case of polar binary systems and more especially whenever strong specific interactions occur between the polymer and the probe (PVF_2 with dipolar aprotic solvents for instance). Nonmonotonous variations of ln Ω_1^∞ versus T^{-1} are actually observed for PVF_2 and butanone, dimethyl sulfoxide, and propylene carbonate (Figure 1). The maximum at about 190 °C, which occurs for the two first solutes, may be ascribed to the weakening of specific polymer–probe interactions with increasing temperature. The minimum at about the same temperature, which occurs for propylene carbonate, may result from an increase of the difference of the free volume between the probe and the polymer close to the phase separation. For these three special cases, the $\overline{\Delta H}_1^\infty$ values were derived from the Ω_1^∞ variations below 190 °C.

Correlation Analysis of the $\overline{\Delta H}_1^\infty$ Variations with Probe Polarity. The partial molar enthalpy of mixing, $\overline{\Delta H}_1^\infty$, obviously results from *all* the various polymer–probe

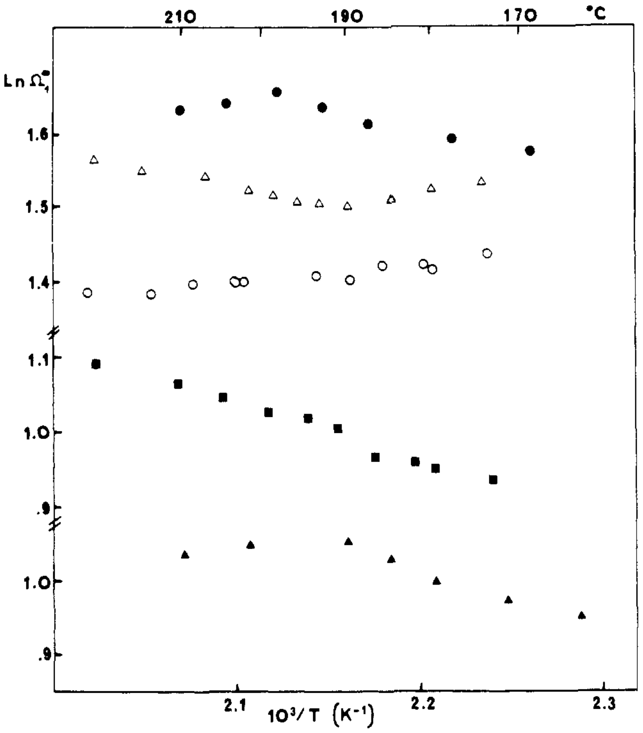

Figure 1. Temperature dependence of ln Ω_1^∞ for the interactions of PVF$_2$ with butanone (●), propylene carbonate (△), γ-butyrolactone (○), dimethylformamide (■), and dimethyl sulfoxide (▲).

interactions, which may be readily identified as nonspecific and specific ones.[26,27]

Nonspecific van der Waals interactions include the London dispersive ones (random dipole–induced dipole) and the Keesom (dipole–dipole) and Debye (dipole–induced dipole) dipolar ones. The polarizability P or the molecular refraction MR (see the Experimental Section) and the dipole moment μ of the probes may be considered unambiguously as good descriptors for the former and for the two latter types of interactions, respectively, since their choice rests upon sound theoretical grounds.[27,28]

Specific interactions include essentially hydrogen bonding and weaker electronic donor–acceptor (EDA) interactions, leading possibly to the formation of a charge-transfer complex. They are currently described within a host of empirical polarity scales, more or less linearly correlated and which involve unfortunately in most cases more than one well-defined type of interaction.[27] According to our opinion the hydrogen bonding accepting (HBA) and donating (HBD) strengths of the solutes are best measured by the empirical solvatochromic parameters β and α introduced by Taft et al.:[15] they result from a statistical optimization of a series of parameters obtained with a variety of probes, and, more especially, the reliability of β as a good descriptor of Gibbs energy of hydrogen bonding between HBA solvents and HBD solutes has been reemphasized very recently.[29] Moreover, Taft et al. have shown that the Gutmann donor and acceptor numbers DN and AN currently used as polarity parameters of solvents related to EDA interactions also involve significant contribution of the dipolar ones.[30] The values of the electronic energies of the highest occupied molecular orbital (HOMO), ϵ_H, and of the lowest unoccupied one (LUMO), ϵ_L, are clearly related to the donor and acceptor aspects of the EDA interactions, respectively (in a number of cases, they are actually correlated with the ionization potentials and electron affinities of the solvents): ϵ_H and ϵ_L may be thus tentatively chosen as potential descriptors of the probes with respect to this type of interaction.

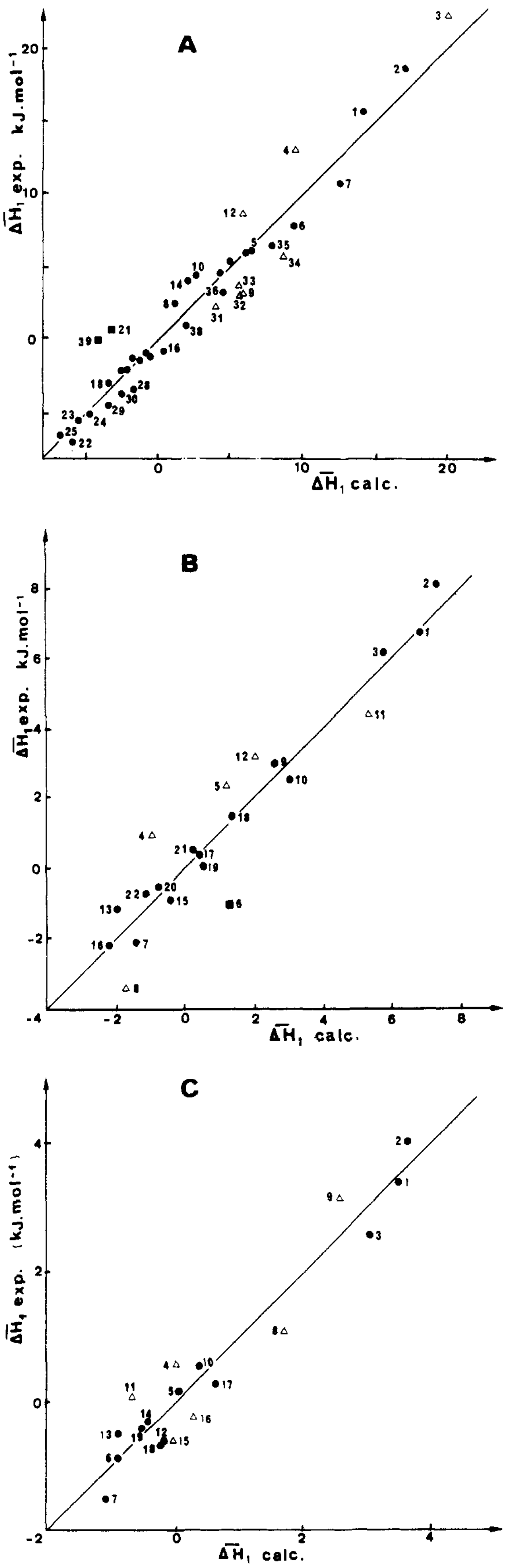

Figure 2. $\overline{\Delta H_1}^\infty$ experimental vs calculated values for the various solute–polymer systems: (●) $\bar{\sigma} < 1$; (△) $1 < \bar{\sigma} < 2$; (■) $\bar{\sigma} > 2$. (A) Solutes–PVF$_2$ according to correlation 6. (B) Solutes–PVAC according to correlation 8. (C) Solutes–PS according to correlation 9.

From a formal viewpoint, the $\overline{\Delta H_1^\infty}$ thermodynamic parameter may be considered as the sum of all the individual contributions of the nonspecific and specific interactions occurring in the binary system. This approach, which necessarily assumes their independence and their additivity, remains obviously empirical, but it allows the analysis of the $\overline{\Delta H_1^\infty}$ variations versus probe polarity through a linear multiparametric equation where the various additive terms are related to a single type of polymer–probe interaction:

$$\overline{\Delta H_1^\infty} = r\mathrm{MR} + m\mu + b\beta + ... \qquad (5)$$

A similar strategy relying on correlation analysis is widely used in physical organic chemistry[31] or for the "Linear Solvation Energy Relationships" developed by Taft et al., for instance.[15]

The coefficients r, m, b, etc., of eq 5 are derived from the $\overline{\Delta H_1^\infty}$ experimental values obtained for a series of probes of known polarity parameters within the usual framework of statistical multidimensional analysis.

For every system the independence of the selected variables is checked for the probe population investigated (see the correlation matrix).

The goodness of the correlation is measured by its multiple regression coefficient, R (n probes), and by its mean-square standard deviation, $\bar{\sigma}$, which has to remain close to the experimental accuracy.

The statistical value of any supplementary term for the improvement of a previous correlation is checked according to the F statistics.[32]

The normalized coefficients r', m', b', etc., derived from the original ones r, m, b, etc., using centered variables to take into account their different variation ranges, directly reflect the sensitivity of the $\overline{\Delta H_1^\infty}$ thermodynamic parameter to the various types of interactions.

Solubility of Volatile Probes in Poly(vinylidene fluoride) (160 < t °C < 210). The correlation matrix including MR, μ, and β as variables, as already selected in our previous study,[5] is given in Table III for the 39 solvents set experimentally involved (Table II). The two descriptors μ and β are not truly independent, and regression analysis led to the correlation

$$\overline{\Delta H_1^\infty}\ (\mathrm{kJ{\cdot}mol^{-1}}) = -4.59 + 0.32\mathrm{MR}\ (\mathrm{cm^3}) - 11.42\beta \qquad (6)$$

$$R(39) = 0.9635 \qquad \bar{\sigma} = 1.84\ (\mathrm{kJ{\cdot}mol^{-1}})$$

In this fairly good correlation (see Figure 2A), the dipole moment term does not appear as a statistically significant descriptor, and the opposite contributions of the molecular refraction and of the hydrogen bond accepting power of the probes are of 55 and 45%, respectively; thus, hydrogen bonding between dipolar HBA probe and PVF_2 acting as a C–H HBD chain appears as the major process for an exothermic mixing process, as already outlined.[5] However, this correlation may be critically discussed from a number of viewpoints:

Until now, we have unfortunately no satisfactory explanation for the strongly negative constant term of the correlation, which appears out of the error domain. The data reduction from experiments carried out with polar probes at relatively high temperature may involve some systematic error on the temperature variations of the second-virial coefficient of the probes calculated from a semiempirical equation essentially valid for weakly polar ones and for a lower temperature range (see the Experimental Section).

Table II
Polarity Parameters of the Various Solutes and Their Partial Molar Enthalpies of Mixing, $\overline{\Delta H_1^\infty}$ with PVF_2

solute	MR, $\mathrm{cm^3}$	$\mu \times 10^{30}$, Cm	β	$\overline{\Delta H_1^\infty}$, $\mathrm{kJ{\cdot}mol^{-1}}$
1. *n*-dodecane	57.8	0	0	15.75
2. *n*-tetradecane	67.0	0	0	18.70
3. *n*-hexadecane	76.3	0	0	22.40
4. *cis*-decalin	43.9	0	0	13.0
5. 1-chlorohexane	34.8	6.6	0.01	6.13
6. 1-chlorooctane	44.0	6.7	0.01	8.04
7. 1-chlorodecane	53.3	6.3	0.01	10.76
8. 1,2-dichloroethane	21.0	4.7	0.08	2.55
9. 1,5-dichloropentane	35.5	7.8	0.08	3.25
10. 1,1,2-trichloroethane	25.9	5.2	0.08	4.52
11. 1,1,2,2-tetrachloroethane	30.6	5.7	0.08	4.60
12. pentachloroethane	35.6	3.5	0.08	8.60
13. di-*n*-propyl thioether	37.8	5.4	0.21	5.49
14. 2,2′-dichlorodiethyl ether	32.0	8.6	0.31	4.04
15. ethyl acetate	22.3	6.3	0.45	−2.08
16. butyl acetate	31.1	6.1	0.44	−0.83
17. ethyl propionate	26.9	5.8	0.42	−0.90
18. 2-butanone	20.7	9.2	0.48	−2.85
19. cyclohexanone	27.9	10.0	0.53	−1.25
20. propylene carbonate	21.5	16.5	0.4	−1.97
21. γ-butyrolactone	20.0	13.7	0.45	0.80
22. *N*,*N*-dimethylformamide	19.9	13.0	0.69	−6.90
23. *N*,*N*-dimethylacetamide	24.3	12.7	0.76	−5.40
24. *N*-methylpyrrolidone	26.8	13.6	0.77	−5.05
25. dimethyl sulfoxide	20.2	13.2	0.76	−6.36
26. tetramethylene sulfone	27.2	15.7	0.4	−1.10
27. hexamethylphosphoramide	47.9	14.3	1.05	−1.30
28. 1,1,3,3-tetramethylurea	32.4	11.2	0.66	−3.27
29. dimethylethyleneurea	30.3	13.6	0.76	−4.40
30. dimethylpropyleneurea	34.9	14.1	0.80	−3.60
31. toluene	31.1	1.1	0.11	2.34
32. ethylbenzene	35.8	1.3	0.12	3.06
33. *m*-xylene	36.0	1.2	0.12	3.77
34. butylbenzene	45.1	1.2	0.12	5.69
35. tetralin	42.9	2.0	0.12	6.57
36. chlorobenzene	31.2	5.1	0.07	3.22
37. *o*-dichlorobenzene	36.0	7.6	0.03	6.07
38. acetophenone	37.7	9.9	0.49	1.13
39. pyridine	24.1	7.3	0.64	0.10

The calculated strongly negative $\overline{\Delta H_1^\infty}$ values for pyridine and γ-butyrolactone are underestimated by more than 2σ. The cyclic ester actually behaves as a probe less polar than it may be anticipated from its μ and β polarity parameters: this feature may be correlated with the fact that it is the poorest solvent of PVF_2 at room temperature.[33]

Among the nine solutes that lead to residuals $|\overline{\Delta H_1^\infty}(\mathrm{calc}) - \overline{\Delta H_1^\infty}(\mathrm{exptl})|$ between one and two $\bar{\sigma}$, the least polar of the aromatic species lead to overestimated $\overline{\Delta H_1^\infty}$ values, as if their polarity measured by a constant $\beta = 0.12$ value was underestimated. The previous correlation may be tentatively improved by discarding the aromatic probes as a homogeneous class. The correlation matrix for the 30 remaining solvents is given in Table III and the regression analysis leads to the amended correlation

$$\overline{\Delta H_1^\infty}\ (\mathrm{kJ{\cdot}mol^{-1}}) = -2.24 + 0.30\mathrm{MR}\ (\mathrm{cm^3}) - 0.18\mu\ (10^{-30}\ \mathrm{Cm}) - 11.00\beta \qquad (7)$$

$$R(30) = 0.9816 \qquad \bar{\sigma} = 1.52\ \mathrm{kJ{\cdot}mol^{-1}}$$

It may appear slightly better than the previous one (see R, σ, and the constant term), but the major feature is the emergence of the μ term as a statistically significant descriptor: μ and β thus account for 10 and 40% of the $\overline{\Delta H_1^\infty}$ variations for this restricted solvent set. An unambiguous and physically sound separation of the con-

Table III
Correlation Matrix between $\overline{\Delta H}_1^{\infty}$ Values and the Basic Physicochemical Variables Used for the Different Systems

poly(vinylidene fluoride)				poly(vinyl acetate)				polystyrene				
	MR, cm^3	μ, Cm	β		MR, cm^3	μ, Cm	ϵ_L, eV		MR, cm^3	μ, Cm	ϵ_L, eV	ϵ_H, eV
μ	−0.56[a] −0.61[b]			μ	0.48			μ	−0.45			
β	−0.46 −0.46	0.79 0.80		ϵ_L	0.16	−0.44		ϵ_L	0.12	−0.54		
$\overline{\Delta H}_1^{\infty}$	0.85 0.85	−0.76 −0.83	−0.79 −0.82	$\overline{\Delta H}_1^{\infty}$	0.57	−0.54	0.84	ϵ_H	0.70	−0.22	0.02	
								$\overline{\Delta H}_1^{\infty}$	0.40	−0.49	0.92	0.19

[a] 39 solvents. [b] 30 solvents.

tribution of dipolar interaction and hydrogen bonding to the mixing process remains, however, difficult since μ and β are rather strongly correlated, but the predominance of the β term is statistically well ascertained.

Solubility of Volatile Probes in Poly(vinyl acetate) ($110 < t$ °C < 150). Except for *n*-alkanes, the $\overline{\Delta H}_1^{\infty}$ values measured for all the solvents tested including aromatic hydrocarbons, chlorinated alkanes, ethers, esters, ketones, and tertiary amides are very weak and often negative (Table IV): chloroform leads to the minimum $\overline{\Delta H}_1^{\infty}$ value of about -3.4 kJ·mol^{-1}. However, they remain significantly higher than those measured in the previous case of the very polar binary system involving PVF_2. With respect to the aprotic solvents studied, the lateral ester group of the polymer chain is a potential site of dipolar and EDA interactions by its *n*-donor properties. MR, μ, and ϵ_L may be thus chosen as pertinent descriptors of the probes, and the corresponding correlation matrix is given in Table III. All the variables are independent, and regression analysis leads to the following correlation (see also Figure 2B):

$$\overline{\Delta H}_1^{\infty}\ (\text{kJ·mol}^{-1}) = 0.46 + 0.19\text{MR}\ (\text{cm}^3) + 0.62\epsilon_L\ (\text{eV}) \qquad (8)$$

$$R(22) = 0.9508 \qquad \bar{\sigma} = 1.00\ \text{kJ·mol}^{-1}$$

The opposite contributions of the MR and ϵ_L terms (ϵ_L is always negative except for *n*-alkanes) are of 36 and 64%, respectively: the *n*-donor character of the ester group thus appears as the major factor favoring probe solubilization in PVAC. The lack of a μ term (not statistically meaningful) may be considered rather surprising since dipole–dipole interactions between PVAC and the dipolar probes could be reasonably expected. Chloroform leads to a high residual of about 1.7σ: hydrogen bonding between this probe ($\alpha = 0.44$) and the ester group, which is not taken into account in the correlation, may likely explain that the calculated $\overline{\Delta H}_1^{\infty}$ value is strongly overestimated with respect to the experimental one. Such a discrepancy is not observed with acetonitrile, which is a definitely weaker H bond donor ($\alpha = 0.19$). Finally, the highest residuals either positive or negative are observed for tetrachloromethane, 1-chlorohexane, and 1,5-dichloropentane and cannot be readily explained on physical grounds.

Solubility of Volatile Probes in Polystyrene ($150 < t$ °C < 190). The experimental results for PS studied with nearly the same solvent set previously involved with PVAC are also given in Table IV. The $\overline{\Delta H}_1^{\infty}$ enthalpies decrease from positive values for *n*-alkanes down to moderately negative ones especially for polychlorinated alkanes: chloroform leads to the minimum $\overline{\Delta H}_1^{\infty}$ value of about -1.6 kJ·mol^{-1}. This characteristic feature emphasizes that PS is actually polar, a fact which most often appears underestimated. In most cases, the aromatic ring may lead to EDA interactions of widely varying energies: it behaves either as a π donor toward σ^* acceptors (chloroalkanes, for instance) or as a π acceptor toward *n*-donors (ethers or esters, for instance). Sulfides are well-known to be better donors than the homologous ethers,[34] and the strong $\overline{\Delta H}_1^{\infty}$ decrease of about 2.6 kJ·mol^{-1} observed when going from *n*-propyl ether to *n*-propyl thioether is an illustrative example of the π acceptor behavior of liquid PS.

The MR, μ, ϵ_L, and ϵ_H descriptors may thus be selected as pertinent variables, and the corresponding correlation matrix for the 19 solvents investigated is given in Table III. Except for MR and ϵ_H, the variables are independent and regression analysis leads to the following correlation (see also Figure 2C):

$$\overline{\Delta H}_1^{\infty}\ (\text{kJ·mol}^{-1}) = 1.17 + 0.07\text{MR}\ (\text{cm}^3) + 0.35\epsilon_L\ (\text{eV}) \qquad (9)$$

$$R(19) = 0.9605 \qquad \bar{\sigma} = 0.47\ (\text{kJ·mol}^{-1})$$

According to this fairly good correlation (see $R(19)$, $\bar{\sigma}$, and the constant term), the opposite contributions of the MR and ϵ_L terms to the $\overline{\Delta H}_1^{\infty}$ variations are about 25 and 75%, respectively. This feature tends to emphasize that the relatively good solvent properties of liquid PS toward a wide variety of probes arise essentially from its π electronic donor specific property. In spite of its statistical goodness, a critical discussion of the correlation on physical grounds is of interest:

It may appear physically unrealistic to describe quantitatively the EDA interactions of PS with all the probes using only their ϵ_L parameter. The lack of any ϵ_H term in the correlation (π acceptor behavior of PS) may result from the fact that ϵ_H, whose variation range is rather narrow, is a roughly linear decreasing function of MR (see previous correlation matrix).

Five probes lead to residuals between one and two σ and more especially chloroform and acetonitrile: these two species are moderate H bond donors, and weak hydrogen bonding may likely occur with PS. The overestimated calculated $\overline{\Delta H}_1^{\infty}$ values may thus arise from the lack of any hydrogen bonding term in the correlation. Some results of our laboratory related to alcohol probes strongly support the existence of hydrogen bonding as a negative contribution to the observed $\overline{\Delta H}_1^{\infty}$ values.[17]

Reliability and Shortcomings of the Enthalpic Correlations. Comparison to the previous correlations shows that, for the three systems investigated, the dispersive interactions that are operative in all cases and are measured by the MR term afford systematically a positive contribution to the enthalpy of mixing and are thus unfavorable to the solubilization process. According to the order of the numerical coefficients *r* of the MR descriptor, $r(PVF_2) > r(PVAC) > r(PS)$, these effects

Table IV
Polarity Parameters of the Various Probes and Their Partial Molar Enthalpies of Mixing with Polystyrene and Poly(vinyl acetate)

					$\overline{\Delta H_1^\infty}$, kJ·mol^{-1}	
solute	MR, cm^3	$\mu \times 10^{30}$, Cm	ϵ_L, eV	ϵ_H, eV	PS	PVAC
1. *n*-hexane	29.9	0	0.94	−12.81	3.4	6.7
2. *n*-heptane	34.6	0	0.39	−12.68	4.04	8.1
3. cyclohexane	27.7	0	0.09	−13.12	2.6	6.15
4. tetrachloromethane	26.4	0	−10.61	−14.35		1.0
5. 1-chlorohexane	34.8	6.6	−9.76	−12.79	0.6	2.40
6. 1,5-dichloropentane	35.5	7.8	−9.8	−12.62	0.2	−1.0
7. 1,2-dichloroethane	21.0	4.7	−9.82	−13.5	−0.87	−2.07
8. chloroform	21.0	3.4	−10.3	−14.0	−1.6	−3.4
9. tetrahydrofuran	20.0	6.0	−2.7	−13.4		3.0
10. dioxane	21.6	1.5	−2.5	−12.9	1.15	2.5
11. di-*n*-propyl ether	31.7	4.4	−1.96	−13.36	3.2	4.37
12. di-*n*-propyl thioether	37.8	5.4	−9.3	−12.61	0.6	3.23
13. acetone	16.2	9.6	−9.1	−12.93		−1.1
14. 2-butanone	20.7	9.2	−9.11	−12.85	0.12	−0.73
15. cyclohexanone	27.9	10.0	−9.04	−12.7	−0.6	
16. ethyl acetate	22.3	6.3	−8.46	−13.37		−0.9
17. acetonitrile	11.1	13.1	−7.9	−13.8	−0.48	−2.17
18. *N*,*N*-dimethylformamide	19.9	13.0	−8.3	−13.04	−0.29	−0.51
19. *N*,*N*-dimethylacetamide	24.3	12.7	−8.1	−13		0.5
20. dimethyl sulfoxide	20.2	13.2	−8.9	−12.7		−0.7
21. benzene	26.2	0	−8.3	−12.8	−0.56	0.4
22. toluene	31.1	1.1	−8.27	−12.63	−0.20	1.5
23. ethylbenzene	35.8	1.3	−8.2	−12.6	0.30	
24. chlorobenzene	31.2	5.1	−9.75	−12.6	−0.65	0.1
25. pyridine	24.1	7.3	−9.3	−12.8	−0.40	

are minimum for PS, and this feature may be considered as self-consistent with the highest polarizability of its aromatic structure. However, it may be emphasized that MR is quite collinear with the molar volume, V, for most of the solvents[18] and more precisely for our probes $R(39) = 0.97$ for the solvent set used for PVF$_2$ for instance. The positive MR contribution may be considered alternatively as a measure of cavitation effects necessary to create a hole and accommodate a probe molecule in the liquid polymeric phase: the bulkier the probe, the less its solubility.

In spite of the lack of any μ term in the previous correlations, the regression coefficient between the $\overline{\Delta H_1^\infty}$ enthalpies and the dipole moment of the probes, as given in the correlation matrixes, is definitely strong for PVF$_2$ (−0.80) and weak but still statistically meaningful for PVAC (−0.54). Dipolar interactions for these two systems are very probable and their greater influence for PVF$_2$ is in good agreement with the relative polarities of the two polymers measured either by their average dipole moment for repeat unit ($\hat{\mu}$) derived from dielectric measurements or by their "apparent local dipole moment" (μ') derived from solvatochromic ones:[35] PVF$_2$, $\hat{\mu} = 2.01$ D and $\mu' = 4.8$ D; PVAC, $\hat{\mu} = 1.8$ and $\mu' = 2.9$ D.

Finally the discrepancies observed in some cases between experimental and calculated $\overline{\Delta H_1^\infty}$ values obviously weaken the reliability and the physical value of the enthalpic correlations. It should be remembered that polarity parameters such as MR, μ, and ϵ_L, for instance, are molecular properties that obviously do not include any geometric and steric factors, which may become of major importance in the development of specific interactions for some solvent–polymer systems.

Polymer–Polymer Compatibility and Enthalpic Correlations. Negative $\overline{\Delta H_1^\infty}$ values reflect strong specific interactions between the solvent 1 and the polymer 2: potential compatibility between the corresponding polymer 1 (carrying repeating units of the same chemical structure as solvent 1) and polymer 2 may be thus expected, and the previous enthalpic correlations are thus of definite interest as a predictive or interpretative tool in the technologically important field of polymer blends.[5]

The miscibility of PVF$_2$ with some poly(alkylacrylate and methacrylates), with poly(vinyl acetate), and with poly(vinyl methyl ketone)[36] is in good agreement with the negative $\overline{\Delta H_1^\infty}$ values observed for ester and ketone solvents in liquid PVF$_2$ (see Table II). Moreover, as already noticed,[5] tertiary amides lead to the lowest $\overline{\Delta H_1^\infty}$ values (see Table II), suggesting potential compatibility of PVF$_2$ with the corresponding tertiary amide polymers: this prediction was successfully checked with a series of polymers such as poly(*N*-vinylpyrrolidone), poly(*N*-propionylethylenimine), and others.[37] In quite a similar way, polymers carrying phosphonamide, tetrasubstituted urea, or sulfoxide functions (see HMPA, TMU, DMEU, DMPU, and DMSO in Table II) could be potentially miscible with PVF$_2$. In the last case, however, some preliminary experiments carried out with atactic poly(propylene sulfoxide)[39] proved to be disappointing: the observed biphasic structure of the blends may result from steric hindrance at the sulfoxide function, an unfavorable factor for the development of specific interactions, which is not obviously taken into account on the model system PVF$_2$–DMSO.

The compatibility noticed between the two statistical copolymers ethylene–vinyl acetate and chlorinated polyethylene[38] may result at least partly from EDA interactions between the ester and the halogenated units, since chlorinated solvents ($C_2H_4Cl_2$, $CHCl_3$, etc.; see Table IV) actually lead to the lowest $\overline{\Delta H_1^\infty}$ values with liquid PVAC.

Conclusion

The quantitative analysis of the thermodynamics of mixing of volatile probes with liquid polymers in terms of probe structure remains obviously an ultimately important goal far from being reached. In spite of the lack of theoretical grounds, correlation analysis may appear at least as any efficient and reliable empirical approach to point out some major trends from a body of experimental data where most of the information cannot be easily extracted by any other way. The results thus obtained suggest the two following concluding remarks:

The correlations derived from the experimental results are very significant on statistical grounds, and they may be safely used as a predictive tool. As already noticed,[5] they are of definite interest in important fields such as polymer–polymer compatibility as modeled by a polymer–solute system (see above) or for the definition of a "local polarity" scale for liquid polymers, which may prove useful for all the systems involving low molecular weight host species in polymeric matrixes.

The physical meaning of the correlations may appear somewhat ambiguous since they depend essentially on the preliminary and difficult choice of the descriptors of the probes, which may be more or less correlated or include various aspects of the polarity. In most unfavorable situations, the descriptor leading to the best correlation on statistical grounds may not be the most relevant and illuminating on physical ones. More reliable descriptors may likely emerge from the always increasing studies on solute–solvent interactions and on the concept of polarity.

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Registry No. PVF$_2$, 24937-79-9; PVAC, 9003-20-7; PS, 9003-53-6; *n*-dodecane, 112-40-3; *n*-tetradecane, 629-59-4; *n*-hexadecane, 544-76-3; *cis*-decalin, 493-01-6; 1-chlorohexane, 544-10-5; 1-chlorooctane, 111-85-3; 1-chlorodecane, 1002-69-3; 1,2-dichloroethane, 107-06-2; 1,5-dichloropentane, 628-76-2; 1,1,2-trichloroethane, 79-00-5; 1,1,2,2-tetrachloroethane, 79-34-5; pentachloroethane, 76-01-7; di-*n*-propyl thioether, 111-47-7; 2,2′-dichlorodiethyl ether, 111-44-4; ethyl acetate, 141-78-6; butyl acetate, 123-86-4; ethyl propionate, 105-37-3; 2-butanone, 78-93-3; cyclohexanone, 108-94-1; propylene carbonate, 108-32-7; γ-butyrolactone, 96-48-0; *N,N*-dimethylformamide, 68-12-2; *N,N*-dimethylacetamide, 127-19-5; *N*-methylpyrrolidone, 872-50-4; dimethyl sulfoxide, 67-68-5; tetramethylene sulfone, 126-33-0; hexamethylphosphoramide, 680-31-9; 1,1,3,3-tetramethylurea, 632-22-4; dimethylethyleneurea, 80-73-9; dimethylpropyleneurea, 7226-23-5; toluene, 108-88-3; ethylbenzene, 100-41-4; *m*-xylene, 108-38-3; butylbenzene, 104-51-8; tetralin, 119-64-2; chlorobenzene, 108-90-7; *o*-dichlorobenzene, 95-50-1; acetophenone, 98-86-2; pyridine, 110-86-1; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; cyclohexane, 110-82-7; tetrachloromethane, 56-23-5; chloroform, 67-66-3; tetrahydrofuran, 109-99-9; dioxane, 123-91-1; di-*n*-propyl ether, 111-43-3; acetone, 67-64-1; acetonitrile, 75-05-8; benzene, 71-43-2.