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Gas–Liquid Chromatography Study of Poly(vinylidene fluoride)–Solvent Interactions. Correlation Analysis of the Partial Molar Enthalpy of Mixing with Probe Polarity

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ABSTRACT: The partial molar enthalpies of mixing at infinite dilution $\Delta\bar{H}_1^{\infty}$ of liquid poly(vinylidene fluoride) (PVF_2) have been measured by gas–liquid chromatography within the temperature range 165–205 °C for 20 aliphatic aprotic probes of widely different polarities. The $\Delta\bar{H}_1^{\infty}$ variations with probe chemical structure may be analyzed with a linear multiparametric correlation that involves probe polarizability P, dipole moment μ, and hydrogen bond accepting power β (Taft's empirical parameter) to estimate the respective contribution of apolar dispersive (P), dipolar (μ), and hydrogen bond (β) interactions to the total enthalpy of the mixing process: $\Delta\bar{H}_1^{\infty}$ (kcal·mol^{-1}) = $0.175P$ (cm^3 × 10^{-24}) − 0.350μ (D) − 2.35β. Besides its major interest as a forecast method, such a correlation, which emphasizes the role of the hydrogen bond donating power of PVF_2 toward basic probes, leads to a better comprehensive analysis of solvation mechanism at a molecular level, to new approaches of PVF_2 miscibility with carbonylated polymers, and finally to a definition of PVF_2 polarity in terms of the numerical coefficients of the P, μ, and β terms.

Introduction

Gas–liquid chromatography (GLC) has been well-known for a long time for providing a useful and versatile technique for the study of the thermodynamics of interactions of binary systems where the two components show wide differences in volatility.[1] As a specific case, polymer–solvent interactions in the liquid state have received great attention within the past decade,[2,3] and a very recent critical comparison of dynamic GLC and static calorimetric data has confirmed the good reliability of the GLC technique and reemphasized its interest.[4]

For a given polymer, the experimental data obtained over a wide temperature range may be readily analyzed with the Flory–Huggins theory, and they lead to a number of important thermodynamic parameters (Ω_1^{∞}, χ_{12}, $\Delta\bar{H}_1^{\infty}$, etc.) for a series of probes. The crucial problem of outstanding importance is obviously to correlate the characteristic variations of these parameters with probe structure in order to gain insight into the various types of polymer–solvent interactions at a molecular level. The purpose of this work is to analyze in a quantitative way the variation of the partial molar heat of mixing at infinite dilution, $\Delta\bar{H}_1^{\infty}$, of a series of various probes in the condensed state with a selected polymer within a general framework similar to the "linear solvation energy relationships" recently developed by Taft et al.[5] through the general equation

$$\Delta\bar{H}_1^{\infty} = aP + b\mu + c\alpha + d\beta \qquad (1)$$

The $\Delta\bar{H}_1^{\infty}$ values may be tentatively correlated with probe polarity parameters P, μ, α, and β through a linear multiparametric equation where the various additive terms are related exclusively to a given type of polymer–solvent interaction: nonpolar dispersive forces (polarizability P), dipolar interactions (dipole moment μ), and hydrogen-bonding interactions (hydrogen bond donating and accepting powers α and β, respectively; empirical parameters in Taft's scale[5]).

Such a strategy may appear most promising since it offers definite advantages over previous approaches for a number of reasons: (a) its general validity, especially for polar systems where strong specific interactions may lead to negative $\Delta\bar{H}_1^{\infty}$ values (the popular Hildebrand solubility parameter theory is not applicable for these systems,[6,7] and the more sophisticated concept of the three-dimensional solubility parameter has been already shown to be of poor efficiency in this field[8,9]); (b) the lack of any normalization of the experimental data with respect to apolar model polymers used as reference systems which do not show the specific interactions that actually occur in the systems under study (see for instance the pure base method first introduced by Martire et al.[10] in GLC studies on low molecular weight compounds and more recently transposed for measurement of hydrogen-bonding interactions in polymeric systems[11,12]); (c) the choice of the partial molar enthalpy of mixing $\Delta\bar{H}_1^{\infty}$ instead of the partial molar enthalpy of dissolution ΔH_s^{∞} previously considered in several works[12–15] (ΔH_s^{∞} is actually a composite thermodynamic parameter that includes the latent heat of vaporization of the probe solute ($\Delta H_s^{\infty} = \Delta\bar{H}_1^{\infty} - \Delta H_v$), which is the major term in most cases. ΔH_s^{∞} cannot thus be taken as a reliable measure of polymer–solute interactions).

Because of its strongly dipolar local structure and its definite technological interest as a macromolecular engineering material, poly(vinylidene fluoride) was selected as a representative polar polymer.

Experimental Section

Probe Molecules and Polymeric Stationary Phase. The alkanes and chloroalkanes of the best "chromatography" grade were used as received. All the other solvents were purified by distillation over convenient drying reagents according to literature procedures[16] and stored over 4-Å molecular sieves. PVF_2, a Kynar 461 sample supplied by Penwalt Corp., was purified by precipitation into water from its dimethylformamide (DMF) solution and vacuum-dried: $\bar{M}_w = 2.75 \times 10^5$ from intrinsic viscosity in dimethylacetamide at 25 °C according to Welch,[17] $t_m = 160.5$ °C (DSC measurement at a heating rate of 10 °C min^{-1}).

Chromatographic measurements were carried out on an Intersmat IGC 15 apparatus fitted with a catharometer, and the general procedure is identical with that previously described.[18] Three different columns were used (0.25-in. stainless steel tubing of 120-cm length) containing 0.635, 0.180, and 0.435 g of PVF_2 deposited from DMF solution onto Fluoropak 80 (40–50 mesh), HMDS-treated glass beads (specific surface area of 0.016 m^2·g^{-1}), and Chromosorb W (60–80 mesh AW-DMCS), respectively. The column loading was systematically checked by Soxhlet extraction and by calcination. The Fluoropak column, in spite of its good performances with respect to polar probes as shown by the high symmetry of their elution peaks, yields probably the least reliable data because it has the highest inaccuracy of polymer weight: PVF_2 extraction may be incomplete because of irreversible adsorption on the support of similar structure, and calcination is

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Table I
Polarizability P, Dipole Moment μ, and Hydrogen Bond Accepting Power β of Pure Solutes at 25 °C and Partial Molar Heat of Mixing $\Delta\bar{H}_1^\infty$ of the Various Solute–PVF$_2$ Systems

					$\Delta\bar{H}_1^\infty$ ± 0.1, kcal·mol^{-1}			
	solute	$P \times 10^{24}$, cm^3	μ, D	β	exptl	(5)	calcd	(6)
1	*n*-dodecane	22.9	0	0	3.90		4.01	
2	*n*-tetradecane	26.0	0	0	4.47		4.55	
3	*n*-hexadecane	30.3	0	0	5.40		5.30	
4	1,2-dichloroethane	8.34	1.40	0	1.2	0.31		0.97
5	1,1,2,2-tetrachloroethane	12.15	1.71	0	1.7	0.73		1.53
6	pentachloroethane	14.11	0.95	0	2.3	1.69		2.14
7	1-chlorooctane	17.45	2.1	0	1.9	1.33		2.32
8	1-chlorodecane	21.13	1.9	0	2.6	2.13		3.03
9	2-butanone	8.24	2.70	0.48	−0.4	−0.77		−0.63
10	cyclohexanone	11.05	3.01	0.53	−0.2	−0.53		−0.36
11	1,2-dimethoxyethane	9.56	1.71	0.41	0.1	0.27		0.13
12	bis(2-methoxyethyl) ether	13.80	1.97	(0.4)	0.6	0.80		0.77
13	ethyl acetate	8.83	1.78	0.45	−0.6	0.09		−0.13
14	dimethylformamide	7.85	3.86	0.69	−1.7	−1.79		−1.60
15	dimethylacetamide	9.57	3.72	0.76	−1.3	−1.38		−1.42
16	*N*-methylpyrrolidone	10.56	4.09	0.72	−1.8	−1.50		−1.39
17	dimethyl sulfoxide	7.94	3.9	0.76	−1.6	−1.80		−1.75
18	tetramethylene sulfone	10.77	4.81	(0.39)	−0.3	−2.06		−0.72
19	propylene carbonate	8.47	4.94	0.40	0.2	−2.57		−1.18
20	γ-butyrolactone	7.91	4.12	0.49	0.4	−2.00		−1.21

not possible for this fluorinated support.

The specific retention volumes V_g° were independent of sample size over the range 0.001–0.1 μL. The conditions of infinite dilution of the solute were simulated by introducing vapor–air mixtures, leading to a measurable signal. In the same way, the V_g° values were also independent of the gas vector flow rate within the range 8–30 mL·min^{-1}.

Results and Discussion

Data Reduction. The specific retention volumes at infinite dilution V_g° were measured between 165 and 205 °C for 20 aprotic solutes of widely different polarity: systematic comparison of the experimental data obtained with the three columns leads to an average accuracy of about ±1.5%.

The activity coefficients at infinite dilution Ω_1^∞ based on weight fraction were derived from the corresponding V_g° values according to Patterson et al.[19]

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

where subscript 1 refers to the 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. In most case, P_1° is calculated from the Antoine equation

$$\log P_1^\circ = A - B/(t + C) \qquad (3)$$

where the constants A, B, and C are taken from Dreisbach compilation[20] or directly from the literature.[21] The B_{11} values are calculated from the relation given by O'Connell and Prausnitz[22] applied to literature data.[23] The importance of the second term in eq 2, which accounts for the nonideality of the probe vapor, is worth emphasizing:[19] if this correction actually remains negligible for alkanes showing very high activity coefficients (contribution of 0.2% to ln Ω_1^∞ for hexadecane, for instance), it may reach much higher values for dipolar solvents showing much lower Ω_1^∞ values (contribution of 12% to ln Ω_1^∞ for DMF, for instance).

The partial molar heat of mixing at infinite dilution $\Delta\bar{H}_1^\infty$ may be directly derived from the temperature dependence of Ω_1^∞ according to

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

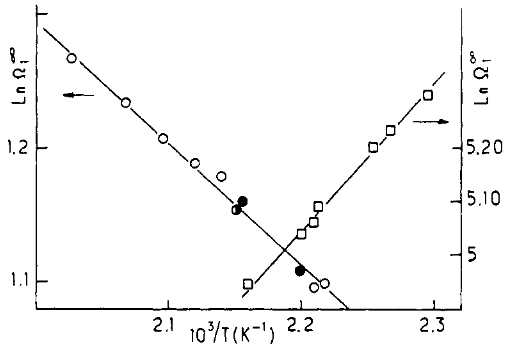

Figure 1. Temperature dependence of the weight-fraction activity coefficient: (□) *n*-hexadecane; (○, ●, and ◑) dimethylformamide on columns 1, 2, and 3, respectively.

Linear variations to ln Ω_1^∞ vs. T^{-1} are observed within the range 165–205 °C: see Figure 1 for hexadecane and DMF as representative nonpolar and dipolar solutes. The average absolute error on $\Delta\bar{H}_1^\infty$ values determined from at least seven measurements at different temperatures may be estimated as ±0.1 kcal·mol^{-1}.

The values of the polarizability P, dipole moment μ,[16,24] and hydrogen bond accepting power β[25] were calculated or taken from literature compilation. The goodness of the linear multiparametric correlation was determined by the total regression coefficient R (n solvents) and the least-squares standard deviation $\bar{\sigma}$.

Partial Molar Enthalpies of Mixing $\Delta\bar{H}_1^\infty$. The experimental results given in Table I may suggest the following comments:

(a) For some common probes allowing direct comparison (correction with the B_{11} term either is negligible or has been performed) such as tetradecane, 1-chlorooctane, 1-chlorodecane, and cyclohexanone, our $\Delta\bar{H}_1^\infty$ values are in very good agreement with those previously obtained by DiPaola-Baranyi et al.[26] in spite of significant differences in the primary V_g° values; the actual polymer weight in the column, which is the main source of error for the V_g° values, does not affect $\Delta\bar{H}_1^\infty$ in the same way, as derived according to eq 4. To the best of our knowledge, there is unfortunately no static calorimetric measurements on the same systems to compare with GLC results.

(b) Alkanes, and to a lower extent chloralkanes, show high positive $\Delta\bar{H}_1^\infty$ values, in good agreement with the

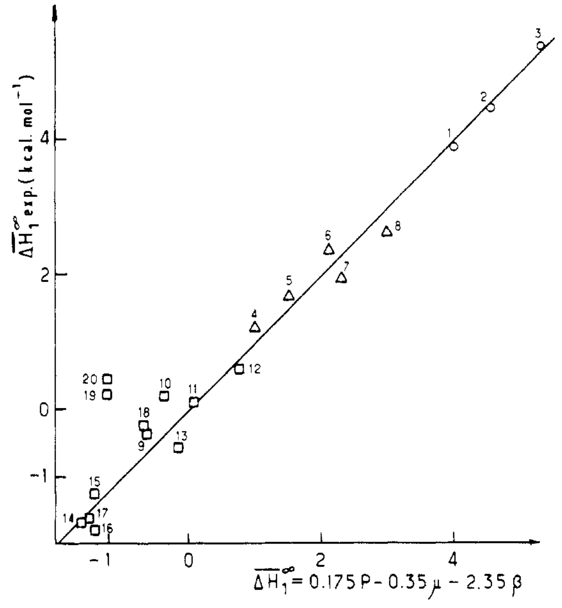

Figure 2. $\Delta\bar{H}_1\infty$ experimental vs. calculated values for the various solute–PVF$_2$ systems according to correlation 6: (○) alkanes; (△) chloroalkanes; (□) oxygenated solvents.

well-known insolubility of PVF$_2$ in these apolar solvents.

(c) For the more polar oxygenated solvents, the $\Delta\bar{H}_1^\infty$ values are strongly decreased and lie within the range +0.5 to −1.8 kcal·mol^{-1}: tertiary amides and dimethyl sulfoxide lead to strongly negative values, in good agreement with the solubility of PVF$_2$ in these highly dipolar solvents.[17]

Correlation Analysis of the $\Delta\bar{H}_1^\infty$ Values with Probe Polarity: $\Delta\bar{H}_1^\infty = f(P,\mu,\beta)$. The preceding results show that dipolar interactions are of definite importance in the mixing process. Stepwise regression analysis on $\Delta\bar{H}_1^\infty$ values vs. the polarizability P and the dipole moment μ for all the solutes except γ-butyrolactone and propylene carbonate leads to correlation 5

$$\Delta\bar{H}_1^\infty\ (\text{kcal·mol}^{-1}) = 0.175P - 0.820\mu$$

$$R(18\ \text{solv}) = 0.9792$$

$$\bar{\sigma} = 0.50\ \text{kcal·mol}^{-1} \tag{5}$$

This correlation, which reasonably accounts for the general trends of the $\Delta\bar{H}_1^\infty$ variations, is not however quite satisfactory since it systematically leads to underestimated $\Delta\bar{H}_1^\infty$ values for n-chloroalkanes and to overestimated values for most of the oxygenated probes. Moreover, all the oxygenated solutes are aprotic hydrogen bond acceptors (HBA) at the ether, carbonyl (carbonate, ester, ketones, and tertiary amides), sulfoxide, or sulfone functions. We thus performed a stepwise three-parameter regression analysis on the experimental data, introducing Taft's β empirical parameter as a measure of the hydrogen bond accepting power of the solute

$$\Delta\bar{H}_1^\infty\ (\text{kcal·mol}^{-1}) = 0.175P - 0.350\mu - 2.35\beta$$

$$R(16\ \text{solv}) = 0.9923$$

$$\bar{\sigma} = 0.20\ \text{kcal·mol}^{-1} \tag{6}$$

The role of the hydrogen-bonding term in this good correlation given in Figure 2 has to be emphasized:

(a) The improvement of the correlation (see R and $\bar{\sigma}$ values) by the introduction of this third polarity β term is meaningful: according to "f statistics"[27] applied to correlations 5 and 6, there is more than 99% probability that the observed improvement is physically significant.

(b) Statistical analysis[28] of the numerical coefficients a = 0.175, b = −0.35, and c = −2.35 shows that the contributions of apolar dispersive forces, dipolar interactions, and hydrogen bonding to the partial molar enthalpy of mixing are about 50, 20, and 30%, respectively. Besides dipolar interactions hydrogen bonding thus appears to contribute significantly to yield an exothermic mixing process: this rather unexpected feature implies that PVF$_2$ behaves as a C–H hydrogen bond donor of sufficient strength. It is well-known that structures characterized by CF$_2$H groups where the hydrogen and fluorine atoms belong to the same carbon may exchange hydrogen bonds with basic reagents: this is for instance the case of 1-hydro-n-perfluoroheptane in acetone, dioxane, and triethylamine.[29] Fluorine has indeed the higher electronegativity[30] and it may be resonably assumed that the CF$_2$ group may induce sufficient polarization of the $C^{\delta-} \leftarrow H^{\delta+}$ bond at the α-carbon atom to enhance its ability to act as a hydrogen bond donor. The spectroscopic results obtained on similar CH$_2$CX$_2$/HBA structures (X = Cl, F) for low molecular weight model systems or the corresponding polymer blends also support this assumption.[31,32]

Limits and Shortcomings of the Correlation. This linear multiparametric analysis may be critically discussed from a number of viewpoints:

(a) The separation of the different types of probe–polymer interaction into additive contributions, whereas they may cooperate in a nonindependent way, has obviously no sound theoretical grounds. However, this approach may find its justification as a useful and versatile empirical method in its ability to correlate and rationalize all the experimental results within a self-consistent framework. Such a strategy is obviously the underlying philosophy in correlation analysis, which raises continuously increasing interest in all the fields of physical organic chemistry.[33]

(b) The choice of the polarity parameters to measure quantitatively and exclusively the various types of probe–polymer interactions is very important. If the polarizability P and the dipole moment μ, already considered in a number of works,[12-15] cause no problem, the selection of an empirical parameter related to the HBA power of the solute is much more critical. After a review of the various basicity scales available, Taft et al.[5] concluded that their β scale was definitely the most reliable and especially better than that defined by the popular Gutman Solvent donicity.[5] The choice of the β values remains however more ambiguous since they are continuously amended and may vary from Taft's group to other workers.[34] In this work, the more recent data set of Taft et al.[25] was used, and slight variations of these values are of minor importance.

(c) The probes that do not fit correlation 6 weaken its general validity. The goodness of the correlation is obviously dependent on the accuracy of the $\Delta\bar{H}_1^\infty$ measurements and on the reliability of the β literature data, but for a number of polar solutes the differences between the observed and calculated $\Delta\bar{H}_1^\infty$ values are definitely out of the error domains: this is especially the case for propylene carbonate and γ-butyrolactone, which are poorer solvents of PVF$_2$ than DMF, DMAC, NMP, and Me$_2$SO. These two cyclic solvents, characterized by a high dipole moment (μ > 4 D) and a relatively weak HBA strength (β < 0.5), show much higher $\Delta\bar{H}_1^\infty$ values than expected from correlation 6. They behave as if they were less polar than suggested by their very high dipole moment. Till now we have no satisfactory explanation for such a discrepancy.

However, correlation 6 rests upon a sufficiently high number of probes in order to be statistically significant, and its general trends may be considered as well ascertained.

In our solute selection we avoid two types of solvents that generally show complex behavior: (a) aromatic hydrocarbons, which, according to Taft et al.,[5] may deviate from the solution linear free energy relationship and are better considered separately; (b) hydrogen bond donors, because hydrogen bonding between PVF_2 and HBD probes at the strongly electronegative fluorine atom is not unreasonable (this would imply the addition of a fourth term in correlation 6, using the Taft α empirical parameter to measure the HBD power of the solute[5]).

$$\Delta\bar{H}_1^\infty = aP + b\mu + c\beta + d\alpha \qquad (7)$$

It has to be emphasized that, in most cases, these solvents are actually both hydrogen bond donors and acceptors (like amphiprotic self-associated alcohols for instance): their α and β values are the least reliable[5,25] and lead to more ambiguous results.

Potential Use of the Correlation $\Delta\bar{H}_1^\infty = f(P,\mu,\beta)$ in the Field of Polymer–Polymer Miscibility. Polymer compatibility is a field of outstanding importance from both theoretical and technological points of view.[35] We recently emphasized that a negative $\Delta\bar{H}_1^\infty$ value for a solvent 1–polymer 2 system is strongly in favor of the miscibility of the polymer 1–polymer 2 pair in which the monomeric unit of polymer 1 has the same chemical structure as the model solvent 1: this is experimentally observed for PVF_2 and poly(dimethylacrylamide) (model solvent dimethylacetamide) or poly(*N*-vinylpyrrolidone) (model solvent *N*-methylpyrrolidone).[36] The knowledge of the $\Delta\bar{H}_1^\infty = f(P,\mu,\beta)$ correlation for a given polymer in thus of interest: (a) as forecast tool for the research of miscible polymer systems (according to (6), polymer bearing sulfoxide groups could be a potential compatible partner for PVF_2, for instance); (b) as a mechanistic tool for a better comprehensive analysis of polymer miscibility at a molecular level. The case of PVF_2 miscibility with carbonyl-bearing polymers such as poly(methyl or ethyl acrylates), poly(methyl or ethyl methacrylates), poly(vinyl acetate), or poly(vinyl methyl ketone) is especially illustrative. Spectrometric measurements definitely show that the C=O group is directly involved in specific interactions, but the site of interaction with the PVF_2 chain has not yet been determined unambiguously. Thus Paul et al.[37,38] and Challa et al.[3] suggest that compatibility mainly arises from dipolar interactions, whereas Fowkes et al.[32] prefer "acid–base complexation" involving the CF_2–CH_2 methylene group. For analogous systems involving poly(vinylidene chloride)/poly(ϵ-caprolactone) or model ester–halogenated solvent systems, Prud'homme et al.[31] also emphasize the important contribution of hydrogen bonding at the $-CH_2CCl_2-$ site. Correlation 6 clearly shows that hydrogen bonding is probably more important than dipolar interactions in PVF_2–polyester compatible blends, and the same is obviously true for the similar PVF_2–poly(dimethylacrylamide) or poly(*N*-vinylpyrrolidone) blends previously mentioned.

As an incident point, we observed that neither poly(α-methylene-γ-butyrolactone) nor poly(vinylene carbonate) is compatible with PVF_2. This is consistent with the positive $\Delta\bar{H}_1^\infty$ values for the model systems PVF_2–γ-butyrolactone or propylene carbonate, but it is worh remembering that these very dipolar probes of relative weak basicity do not obey correlation 6.

Potential Use of the Correlation $\Delta\bar{H}_1^\infty = f(P,\mu,\beta)$ for a Polarity Scale of Polymers. The three numerical coefficients *a*, *b*, and *c* of the *P*, μ, and β terms are specific to liquid PVF_2: they define three polarity parameters related to apolar dispersive, dipolar, and hydrogen-bonding interactions. Extension of the measurements to a series of polymers would result in the construction of a comprehensive polarity scale of polymers considering the heat of mixing at infinite dilution in solute–polymer systems as the reference thermodynamic property. Such an approach, which tests the polymer at a local level, affords much more information than a more global polarity definition through a single parameter like dielectric constant, dipole moment, or Hildebrand solubility parameter. It is obviously reminiscent of the concept of the three-dimensional solubility parameter[39] but may appear to rest upon more simple and thus more sound assumptions. With respect to many spectrometric methods that measure polymer polarity through their interaction with some well-defined labeling probe (UV–vis absorption[40] or fluorescence[41] of selected chromophores dissolved in polymer matrices, for instance), the $\Delta\bar{H}_1 = f(P,\mu,\beta)$ correlation shows the definite advantage of a polarity scale independent of solute structure. Finally our definition of polymer polarity may be compared with the recent approach of Fowkes et al.,[32] who combine the cohesive energy density and Drago's parameters to quantify polymer–solute interactions in terms of London dispersive forces and Lewis acid–base interactions, respectively.

Conclusion

The partial molar enthalpies of mixing at infinite dilution of 18 aprotic probes of widely different polarity with PVF_2 may be quantitatively interpreted with a linear three-parameter correlation involving probe polarizability *P*, dipole moment μ, and hydrogen bond accepting power β

$$\Delta\bar{H}_1^\infty\ (\text{kcal}\cdot\text{mol}^{-1}) = 0.175P\ (\text{cm}^3 \times 10^{-24}) - 0.35\mu\ (\text{D}) - 2.53\beta$$

In spite of the lack of sound theoretical grounds and a few shortcomings at the experimental level, this correlation appears to be of major interest from various viewpoints, since besides rationalizing thermodynamic data in a self-consistent framework, it allows one to gain new insights into important fields such as bulk polymer polarities and polymer–polymer miscibility.

Registry No. PVF_2, 24937-79-9; *n*-tetradecane, 629-59-4; *n*-hexadecane, 544-76-3; 1,2-dichloroethane, 107-06-2; 1,1,2,2-tetrachloroethane, 79-34-5; pentachloroethane, 76-01-7; 1-chlorooctane, 111-85-3; 1-chlorodecane, 1002-69-3; 2-butanone, 78-93-3; cyclohexanone, 108-94-1; 1,2-dimethoxyethane, 110-71-4; bis(2-methoxyethyl) ether, 111-96-6; ethyl acetate, 141-78-6; dimethylformamide, 68-12-2; dimethylacetamide, 127-19-5; *N*-methylpyrrolidone, 872-50-4; dimethyl sulfoxide, 67-68-5; tetramethylene sulfone, 126-33-0; propylene carbonate, 108-32-7; γ-butyrolactone, 96-48-0; *n*-dodecane, 112-40-3.

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Inverse Gas Chromatography. 3. Dependence of Retention Volume on the Amount of Probe Injected

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ABSTRACT: A theory is developed for studying the effect of probe concentration on the chromatographic behavior of inverse gas chromatography (IGC) columns. The dependence of retention volume of the probe on the volume of probe injected is linear in the range of routine injections. The slope of the dependence is a function of the reduced retention volume and of the ratio of retention volume and the width of the peak. The theory does not introduce any adjustable parameters. The theory described well the experimental data obtained on three columns loaded with different amounts of polyisobutylene; three flow rates and three alkane probes were used at two different temperatures. The theory allows one to estimate from a single IGC experiment the correction needed for obtaining retention volumes extrapolated to the vanishing concentration of the probe.

In our on-going research on inverse gas chromatography (IGC), we have been trying to improve the experimental precision of the method by developing a new coating technique,[1] by improving the measurement of the flow rate,[2] and by correcting the data for the interaction of the probe with the chromatographic support.[3] In this paper, we will analyze, theoretically and experimentally, the dependence of retention volumes on the amount of the injected probe. Polyisobutylene was used as a model polymer; it has already been studied by a number of researchers.[4-11] Leung and Eichinger[4] have reported, but not analyzed, the dependence of retention volume on the size of the injection.

Theory

Let us assume that the effect of the chromatographic support has been corrected for. Then the retention volume of the probe is related to the distribution coefficient of the probe between the gas phase and the polymer phase. The distribution coefficient is generally concentration-dependent. We will now calculate this dependence using the Flory–Huggins theory of polymer solutions with a constant value of the well-known parameter χ.

In the following, we will use subscript 1 for the probe, subscript 2 for the polymer, superscript l for the liquid phase, and superscript g for the gas phase; c is concentration (g/mL). The Flory–Huggins relation for the change of the Gibbs function in the process of mixing, ΔG_{mix}, reads

$$\Delta G_{\mathrm{mix}} = RT[n_1^{\mathrm{l}} \ln \phi_1^{\mathrm{l}} + n_2^{\mathrm{l}} \ln \phi_2^{\mathrm{l}} + n_1^{\mathrm{l}}\phi_2^{\mathrm{l}}\chi] \qquad (1)$$

where n_i and ϕ_i are the number of moles and volume fraction of the ith component, respectively; RT has its usual meaning. Concentration c_1^{l} is related to the volume fraction as $\phi_1^{\mathrm{l}} = v_1^{\mathrm{l}}c_1^{\mathrm{l}}$, where v_1^{l} is the specific volume of the probe.

At equilibrium, the difference $\Delta\mu_1$ of the chemical potential of the probe in either phase from the chemical potential in the reference state (pure probe, temperature of the column T, saturated vapor pressure P_1^0 at this temperature) is the same $\Delta\mu_1^{\mathrm{l}} = \Delta\mu_1^{\mathrm{g}}$. A routine thermodynamic treatment yields

$$RT \ln (RTc_1^{\mathrm{g}}/M_1P_1^0) - (B_{11} - V_1^{\mathrm{l}})P_1^0 = (\partial\Delta G_{\mathrm{mix}}/\partial n_1^{\mathrm{l}})_{n_{j\neq 1},P,T} \qquad (2)$$

where P_1^0 and M_1 are the saturated vapor pressure and molecular weight of the probe, respectively, V_i^{l} is the molar volume of the ith component, and B_{11} is the second virial coefficient of the probe in the gas phase.

Combination of eq 1 and 2 yields after some rearrangements

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