Study of Polymer–Solvent Interactions by Gas Chromatography. Copolymers of Vinyl Acetate and Vinyl Alcohol with Hydrocarbons and Alcohols

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Synopsis

The specific retention volumes of nine hydrocarbons and 12 alcohols were measured at several temperatures within the range 120–150°C in columns whose stationary phases were poly(vinyl acetate) (PVAc) and four copolymers of vinyl acetate and vinyl alcohol with 94.8, 74.4, 60.9, and 43.4 mol % of vinyl acetate units (mol % VAc). No chromatographic retention for hydrocarbons was detected in columns loaded with poly(vinyl alcohol) (PVA) or a copolymer with 11.9 mol % VAc. The retention trends are discussed and the polymers solubility parameters (δ_2) were computed from the measured Flory–Huggins χ parameters. The copolymers δ_2 values increase almost linearly with decreasing mol % VAc; PVAc, however, has a distinct behavior. The limitations of the approach in the prediction of χ parameters are discussed.

INTRODUCTION

Some years ago Patterson et al.[1] demonstrated that Flory–Huggins polymer (2)–solvent (1) interaction parameters (χ) at infinite dilution of component 1 could be rapidly and precisely measured by gas–liquid chromatography. In spite of the concentration dependence of χ, values measured at infinite dilution are extremely useful as a first guide in the prediction of polymer–solvent compatibility, in the testing of molecular models, and in the study of solvent retention by polymer films.

Interaction parameters may be predicted by means of molecular models with sound theoretical basis; those developed by Prigogine[2] and by Flory,[3] for instance, have been the object of excellent reviews written by Patterson[4] and by Orwoll,[5] respectively. The data required to apply these theories, however, are very difficult to obtain or are not available at all for most of the systems with practical technical interest. Therefore, it is not surprising to find that many authors, with this kind of application in mind, have resorted to the relation proposed by Huggins[6] and by Scott and Magat[7]:

$$\chi = (\nu_1/RT)(\delta_1 - \delta_2)^2 + \chi_s \tag{1}$$

where ν_1 is the solvent molar volume, δ_1 and δ_2 are the solubility parameters of solvent and polymer, respectively, and χ_s is an entropy correction term,

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which is usually considered as a fixed value, between 0.3 and 0.5, for all the systems and temperatures. Solubility parameters for volatile liquids are calculated from liquid density and molar heat of vaporization (ΔH_v) data, referred to the same temperature; in those cases where direct calorimetric information is not available, ΔH_v can be calculated by the Haggenmacher equation,[8] using the Antoine vapor pressure equation coefficients and tabulated critical constants. Polymers solubility parameters have been deduced from swelling,[9] solubility,[10] or viscosity[11] measurements, or have been calculated by the group contributions method.[12]

Di Paola-Baranyi and Guillet[13] demonstrated that gas chromatography provides an advantageous option for the determination of δ_2. Rearrangement of eq. (1) gives

$$\left(\delta_1^2 / RT \right) - \left(\chi / \nu_1 \right) = \left[2\delta_2 / RT \right] \delta_1 - \left[\left(\delta_2^2 / RT \right) - \left(\chi_s / \nu_1 \right) \right] \qquad (2)$$

Since χ_s / ν_1 is negligible when compared with δ_2^2 / RT, a plot of the left-hand side of eq. (2) against δ_1 should yield a straight line with a slope $2\delta_2 / RT$. Equation (2) was used in several opportunities, with gas chromatographic data measured on different polymers[14–19]; excellent straight lines were always obtained, including those cases where the solute probes belonged to several and very different families.

In order to be studied by gas chromatography, a polymer must behave as a truly amorphous liquid. Semicrystalline polymers fulfill this requirement at temperatures lightly higher than their melting points (T_m). Amorphous polymers have to be worked at temperatures 30–50°C above their glass transition temperatures (T_g), since equilibrium between the stationary and the mobile phases is precluded in the neighborhood of T_g by the very slow diffusion of the probe through the bulk of the polymer.

The T_g of the amorphous polymer poly(vinyl acetate) (PVAc) has been reported to be in the range 28–32°C[20]; careful chromatographic studies have shown that temperatures above 80°C are required to reach true thermodynamic sorption equilibrium.[21] Poly(vinyl alcohol) (PVA) is semicrystalline, with melting temperature between 212 and 267°C, depending on the polymer tacticity and purity; the second order transition temperature of the amorphous portion lies between 70 and 80°C.[22]

Copolymers of vinyl alcohol and vinyl acetate can be prepared in several ways[23,24]: (1) partial saponification of PVAc, adjusting the base concentration to give the desired copolymer composition; (2) methoxide-catalyzed transesterification of PVAc in ethanol or methanol, stopping the reaction at the desired composition; (3) acid-catalyzed equilibration of PVAc or PVA in acetic acid–water mixtures, where the end product content of acetyl groups depends on the initial composition of the reaction mixture. The properties of the copolymers are strongly dependent on the preparation method.[22,23] Partial saponification leads to block copolymers with high melting points. The copolymers obtained by method (3) are random, and their melting points decrease linearly as the mole percent of vinyl acetate units (mol % VAc) increases ($T_m = 145$°C for mol % VAc = 10). There is also a monotonous decrease in T_g with increasing the mol % VAc. Copolymers of intermediate T_g and order are prepared by transesterification.

PVAc has been studied by gas chromatography in several opportunities.[14,16,19,21] PVA is not suitable for this type of study, unless the temperature is raised above 200°C, temperature at which decomposition begins. In this work we present the results obtained with PVAc, PVA, and five copolymers as stationary phases, and a group of hydrocarbons and alcohols as solute probes, between 120 and 150°C. PVA was included with comparative purposes; however, as will be shown later, chromatographic retention is null in columns containing PVA or copolymers with low mol % VAc as stationary phases.

EXPERIMENTAL

Materials. PVAc ($\bar{M}_w$ = 500,000) and PVA ($\bar{M}_w$ = 75,000) were obtained from Polyscience, Inc. All the solutes were of chromatographic quality, and were used as received. The chemicals employed in the synthesis of the copolymers and in the preparation of the packings were C. Erba RPE. Chromosorb W 60/80 and Chromosorb W AW DMCS 60/80 were obtained from Johns-Manville.

Preparation of the Copolymers. Two different methods were used.

Method a[24]: The PVA (6 g) was vigorously stirred under a reflux condenser at 40°C with a mixture of glacial acetic acid (V cm^3), water (60 − V cm^3) and concentrated hydrochloric acid (1 cm^3) for 24 h. After cooling, solubility tests with water and with acetone were performed on 0.5 cm^3 samples of reaction mixture. Water insoluble polymers (mol % VAc > 30) were precipitated with distilled water, washed and reprecipitated twice from methanol. Acetone insoluble polymers (mol % VAc < 30) were precipitated with acetone, washed and reprecipitated twice from water. The products were dried in a vacuum oven at 50°C for 72 h. Copolymers with 74.4, 60.9, 43.4, and 11.9 mol % VAc were prepared by this method, by making V = 60, 55, 50, or 40 cm^3 of glacial acetic acid, respectively.

Method b[25]: The PVA (6 g) was vigorously stirred under a reflux condenser at 90–100°C with a mixture of glacial acetic acid (45 cm^3), acetic anhydride (45 cm^3), and pyridine (5 cm^3) for 24 h. After cooling, the polymer was precipitated with water, washed, reprecipitated twice from methanol, and dried in a vacuum oven at 50°C for 72 h. The product contained 94.8 mol % VAc.

Characterization of the Copolymers. The products were analyzed by the saponification method described by Ahmed and Pritchard.[24] Infrared spectra were obtained with a Beckman 4260 IR spectrophotometer, using thin films deposited on barium fluoride or potassium bromide windows. Besides the obvious decrease in the intensity of the broad HO stretching band at 3340 cm^{-1} and increase in the intensity of the carbonyl band at 1734 cm^{-1} as the mol % VAC increased, there was an interesting change in the aspect of the carbonyl band. This band had a shoulder at 1715 cm^{-1} in the spectra of the copolymers; this shoulder was very low for the 94.8 mol % VAC copolymer, but its height increased as the mol % VAc decreased and, finally, the band for the 11.9 mol % VAc copolymer showed a peak at 1715 cm^{-1} with a high shoulder at 1734 cm^{-1}. This behavior has been attributed to hydrogen bonding of the carbonyl group with an adjacent hydroxyl group, and is a

TABLE I
Column Characteristics

Column identification	Stationary phase	Solid support	Weight % of stationary phase	Solvent used to prepare the packing
A1	PVAc	Chromosorb W AW DMCS 60/80	10.00	$CHCl_3$
A2	PVAc	Chromosorb W AW DMCS 60/80	5.02	$CHCl_3$
B	94.8 mol % VAc	Chromosorb W AW DMCS 60/80	10.02	$CHCl_3 + CH_3OH$, 1 : 1
C	74.4 mol % VAc	Chromosorb W AW DMCS 60/80	10.02	$CHCl_3 + CH_3OH$, 1 : 1
D	60.9 mol % VAc	Chromosorb W AW DMCS 60/80	10.00	$CHCl_3 + CH_3OH$, 1 : 1
E1	43.4 mol % VAc	Chromosorb W AW DMCS 60/80	10.01	$CHCl_3 + CH_3OH$, 1 : 1
E2	43.4 mol % VAc	Chromosorb W AW DMCS 60/80	4.58	$CHCl_3 + CH_3OH$, 1 : 1
F	11.9 mol % VAc	Chromosorb W 60/80	9.91	Water
G	PVA	Chromosorb W 60/80	10.64	Water

qualitative indication of the randomness in the distribution of vinyl acetate and vinyl alcohol units in the chain.[23,26] The spectra of block copolymers obtained by saponification of PVAc do not show absorption at 1715 cm^{-1}.

Columns. Salient column characteristics are summarized in Table I. Packings were prepared in rotary evaporator; after vacuum drying at 50°C for 48 h, the free flowing powders were packed by aspiration into 0.25-in. o.d. precoiled stainless steel tubes 1.5 m in length.

Apparatus and Procedure. Measurements were carried out on a Hewlett-Packard 5880A gas chromatograph, equipped with a flame ionization detector. The carrier gas was nitrogen, purified by successively passing through traps containing silica gel, Molecular Sieve 5A, and a commercial packing consisting of a highly active metal supported on a ceramic base. Flow rates were conventionally measured with a soap-bubble buret at the detector outlet; inlet pressures were periodically measured by inserting through the injection port septum the needle of a 10-μL Hamilton syringe that was connected to a mercury manometer. Carrier gas flow rates ranged between 10 and 60 cm^3 min^{-1}, so as to obtain reasonable retention times. Solutes were individually injected, together with a small amount of methane marker, by means of Hamilton syringes, either under the form of vapors (10-μL syringe) or as solutions in a convenient solvent (1-μL syringe). The injection port and the detector were operated at 180 and 200°C, respectively.

Each solute was run at least four times at each temperature. Retention times t_R, were measured in the form described in the sample size effects discussion. Specific retention volumes V_g were calculated from the relation

$$V_g = j(F_f/w)(273.15/T_f)(t_R - t_0)(p_0 - p_w)/p_0 \tag{3}$$

where j is the James–Martin carrier gas compressibility correction factor, p_0 is the outlet (atmospheric) pressure, F_f is the carrier gas flow rate measured at the pressure (p_0) and temperature (T_f) of the flowmeter, w is the mass of polymer within the column, p_w is the water vapor pressure at T_f, and t_0 is the methane retention time.

RESULTS AND DISCUSSION

The injection of 0.005–0.01 μL of pure alcohols (diluted in an appropriate solvent) in columns with PVAc as the stationary phase resulted in tailing peaks; a decrease of 1 or 2 orders of magnitude in sample size, achieved by injecting solute vapors, led to an increase in peak asymmetry. Some years ago Martire and Riedl[27] noticed that for systems with this behavior, characteristic of solute adsorption on the solid support with isotherms that become nonlinear at very low solute concentration, a region of symmetrical peaks is reached by increasing the sample size, and that further increments result in the reappearance of the asymmetry. It is reasonable to assume that the flat portion of a Langmuir type isotherm is reached with the first increment in sample size; as long as the solution process remains linear up to this point, a region of linearity for the total distribution (i.e., adsorption + solution) shall begin at this concentration, resulting in symmetrical chromatographic peaks. Peak asymmetry shall reappear at the solute concentration where the solution process becomes nonlinear. The skew ratio η defined by the expression

$$\eta = (t_m - t_l)/(t_F - t_m) \tag{4}$$

where t_l and t_F are the times read at the intersections of the tangents drawn at the leading and the trailing inflection points with the base line, respectively, and t_m is the peak maximum retention time, was used to measure asymmetry. η values were, typically, 0.5–0.7 for alcohol vapor samples and 0.9–1 for 0.1–0.2 μL liquid samples with tailing increasing for larger sample sizes. When retention times were calculated by the method of Littlewood, Phillips, and Price,[28]

$$t_R = t_l + t_F - t_m \tag{5}$$

variations smaller than 1% were obtained for liquid samples between 0.1 and 2 or 3 μL; eq. (5) has been successfully compared by Conder et al.[29] with other methods for calculating infinite dilution t_R on skewed peaks. Therefore, the criterion adopted to measure the alcohols retention times was to inject four or five liquid samples with sizes within the range 0.2–2 μL, and to apply eq. (5).

A representative group of solutes was studied both on the 5.02 (A2) and on the 10.00% (A1) PVAc loaded columns; no evidence was found for solute adsorption at the gas–polymer interface. The alkanes, on the other side, showed no retention at 135°C in the column containing PVA as the stationary phase (column G), and the net retention times in column F (11.9 mol % VAc copolymer) were short enough as to make their measurement impracticable with ordinary dimensions columns. Inasmuch as no solute adsorption occurs at the gas–PVAc interface and there is no retention at all in PVA or in copolymers with low degree of acetylation, it is legitimate to assume the

CASTELLS AND MAZZA

TABLE II
Specific Retention Volumes V_g (cm³ g⁻¹) for Solute–Polymer Systems at 135° C

Solute	VAc (mol %)				
	100	94.8	74.4	60.9	43.4
n-Nonane	8.15	8.02	5.38	3.51	2.28
n-Decane	13.07	12.93	8.42	5.32	3.46
n-Undecane	20.32	19.05	12.90	7.98	5.22
n-Dodecane	31.71	31.06	19.74	12.12	8.35
n-Tetradecane	73.76	72.48	46.70	27.69	17.51
n-Hexadecane	175.8	201.7	110.8	65.35	38.76
Benzene	13.31	12.52	9.75	6.98	5.15
Toluene	21.10	19.86	15.18	10.67	7.63
Ethylbenzene	31.54	30.70	21.92	15.18	10.68
n-Propanol	16.92	15.18	14.46	12.84	11.98
n-Butanol	27.91	26.72	23.63	20.20	18.56
n-Pentanol	44.59	43.27	37.70	31.61	28.47
n-Hexanol	70.82	67.92	58.68	48.45	42.66
n-Heptanol	111.2	106.5	90.74	73.39	62.51
n-Octanol	173.4	178.2	139.7	108.4	97.25
n-Decanol	417.2	429.6	332.1	245.0	209.6
Isopropanol	10.26	9.15	9.00	7.69	6.94
sec-Butanol	16.82	15.16	14.02	11.77	10.31
tert-Butanol	22.02	19.86	18.21	15.25	13.59
sec-Pentanol	27.00	23.58	21.25	17.43	15.02
Cyclohexanol	102.0	98.97	90.04	77.63	72.78

absence of stationary phase surface effects for the remaining copolymers. This fact was experimentally confirmed for a selected group of solutes by comparing their specific retention volumes in columns E1 and E2, loaded with 10.00 and 4.58% w/w of the 43.4 mol % VAc copolymer.

Specific retention volumes were measured at five (columns B, C, D, and E1) or six (column A1) temperatures equally spaced within the range 120–150°C, and they are available as supplementary material (see supplementary material paragraph at the end of this article). The results at 135°C have been collected in Table II.

Figure 1 is a plot of V_g^x/V_g^{100} against mol % VAc, where V_g^x and V_g^{100} are the specific retention volumes at 135°C for a given solute in the columns containing x mol % VAc copolymer and PVAc, respectively, as stationary phases. The data for n-butane and n-hexadecanol were extrapolated from the correlations ln V_g vs. N (= number of carbon atoms) for n-alkanes and primary alcohols in the different columns (correlation coefficients in excess of 0.9995). Two unexpected characteristics are manifested in this plot.

In the first place, the lower members of both homologous series show a continuous decrease in V_g with decreasing mol % VAc; the higher alkanes and primary alcohols, however, have a maximum V_g at the 94.8 mol % VAc copolymer. There is an inversion point, where $V_g^{100} = V_g^{94.8}$, that occurs at $N = 12$ in the alkane series and at $N = 8$ for primary alcohols. For large solute molecules, therefore, PVAc does not follow the retention trend displayed by the copolymers. The PVA sample employed to prepare the copolymers would have originated, in case of 100% reacetylated, a PVAc with
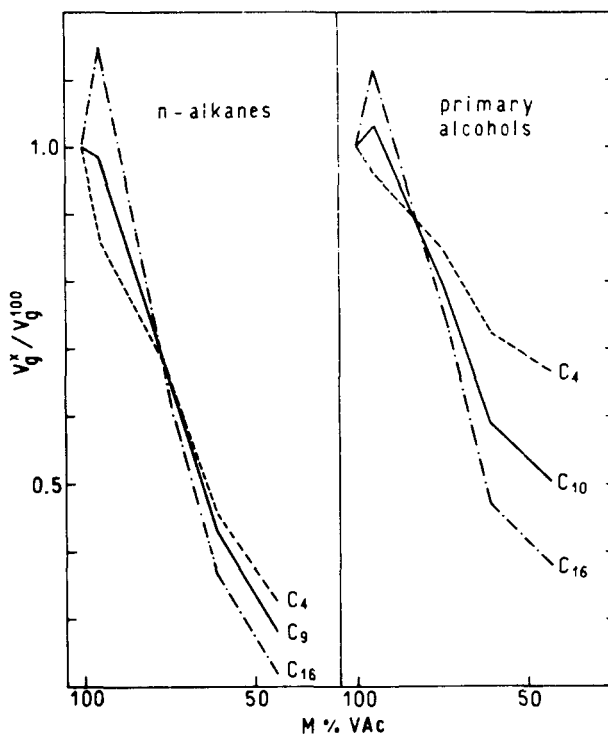
Fig. 1.   Ratio V_g^x/V_g^{100} against mol % VAc at 135°C, where V_g^x and V_g^{100} represent specific retention volumes in columns containing the x mol % VAc copolymer and PVAc, respectively.

$\overline{M}_w = 150{,}000$, against $\overline{M}_w = 500{,}000$ for the PVAc sample utilized in our experiments; no stationary phase molecular size effects can be expected at these molecular weight levels.[30,31] An explanation may be sought in the fact that commercially produced PVAc, obtained at high conversion polymerizations, is usually highly branched, and that most of the branches split off during saponification to PVA, and do not regenerate during reacetylation.[32] Predominantly linear structure may be expected for our copolymers, in contraposition to a high degree of branching for the commercial sample of PVAc; this structural difference could be responsible for the decrease in the solubility of the large solute probe molecules in passing from the 94.8 mol % VAc copolymer to PVAc.

The second peculiarity in Figure 1 is the decrease in the alcohols retention volumes with increasing the free hydroxyl group concentration in the stationary phase; the larger the alcohol molecule, the more notorious this effect. The alcohol solutes most probably interact more strongly with the free HO than with the ester groups in the polymer. However, as the free HO concentration increases the possibilities of hydrogen bonding between polymer chains also increase, thus hindering the entrance of foreign molecules.

Flory–Huggins interaction parameters were calculated with the equation[1]

$$\chi = \ln\left(273.15Rv_2/p_1^0 V_g v_1\right) - 1 - \left(p_1^0/RT\right)\left(B_{11} - v_1\right) \qquad (6)$$

where v_2 represents the polymer specific volume, p_1^0 is the pure volatile component vapor pressure, and B_{11} is the second virial coefficient for the solute–solute interactions in the vapor phase. Vapor pressures were calculated by means of the Antoine equation, using the coefficients compiled by Dreisbach[33] for the hydrocarbons and those cited by Riddick and Bunger[34] for the alcohols; vapor pressures for a few alcohols were interpolated from the experimental data gathered by Jordan.[35] The hydrocarbons molar volumes were computed with the modification of the Racket equation and the coefficients proposed by Spencer,[36] and those of the alcohols by means of Watson's correlation.[37]

Second virial coefficients were calculated by means of the corresponding states equation of McGlashan and Potter,[38] using the critical volumes (V_c) and temperatures (T_c) compiled by Kudchadker et al.[39] The effective carbon number was taken to be the actual number of carbon atoms in the alkane molecule, while the suggestions of Guggenheim and Wormald[40] were followed for the aromatic hydrocarbons. Several solutions,[41-43] using difficult to obtain parameters and relatively high degrees of arbitrariness, have been proposed for the problem of predicting the second virial coefficients of hydrogen bonding vapors. Experimental values for the two propanols and the four butanols at several temperatures have been quoted in the compilation by Dymond and Smith.[44] When the differences between B_{11}/V_c and the first three terms in the equation of McGlashan and Potter are plotted against $(T_c/T)^{4.5}$, a straight line with a slope -0.35 ± 0.04 may be drawn through the points and the origin. It was assumed that this line was representative of

TABLE III
Flory–Huggins χ Parameters for Solute–Polymer Systems at 135°C

Solute	VAc (mol %)				
	100	94.8	74.4	60.9	43.4
n-Nonane	1.973	1.995	2.395	2.823	3.255
n-Decane	2.100	2.101	2.530	2.989	3.420
n-Undecane	2.222	2.294	2.683	3.163	3.588
n-Dodecane	2.364	2.385	2.839	3.327	3.699
n-Tetradecane	2.705	2.715	3.154	3.677	4.135
n-Hexadecane	2.986	2.838	3.437	3.965	4.487
Benzene	0.321	0.419	0.669	1.003	1.307
Toluene	0.457	0.547	0.816	1.169	1.504
Ethylbenzene	0.576	0.639	0.976	1.343	1.695
n-Propanol	0.385	0.516	0.565	0.684	0.760
n-Butanol	0.379	0.438	0.561	0.718	0.803
n-Pentanol	0.410	0.468	0.606	0.783	0.887
n-Hexanol	0.489	0.534	0.680	0.872	0.999
n-Heptanol	0.552	0.599	0.760	0.972	1.132
n-Octanol	0.647	0.618	0.860	1.113	1.222
n-Decanol	0.807	0.772	1.029	1.333	1.490
Isopropanol	0.362	0.501	0.518	0.675	0.777
sec-Butanol	0.313	0.421	0.499	0.674	0.806
tert-Butanol	0.298	0.415	0.501	0.679	0.794
sec-Pentanol	0.336	0.451	0.555	0.753	0.902
Cyclohexanol	0.432	0.449	0.543	0.692	0.756

TABLE IV
Polymers Solubility Parameters at 135°C, Their Temperature Dependence
and Values Extrapolated to 25°C

	VAc (mol %)				
	100	94.8	74.4	60.9	43.4
A. Results at 135°C					
$\delta_2{}^a$	8.73 ± 0.09	8.64 ± 0.10	8.83 ± 0.08	8.96 ± 0.07	9.15 ± 0.08
Correlation coefficient	0.9990	0.9987	0.9991	0.9993	0.9992
$(\chi_s/\nu_1)^b$	0.0031	0.0036	0.0047	0.0062	0.0071
B. Temperature dependence of δ_2					
α^c	10.382	10.129	10.551	10.785	11.025
β^c	0.0122	0.0112	0.0130	0.0138	0.0141
Correlation coefficient	0.989	0.987	0.991	0.993	0.995
δ_2 at 25°C	10.08	9.85	10.23	10.44	10.67

^{a}(cal/cm^3)$^{0.5}$; the error limits are standard deviations based on the least-squares analysis.
^{b}mol/cm^3.
^{c}Constant coefficients in eq. (7).

the behavior of the whole group of alcohols and its slope, in conjunction with the first three terms in the corresponding states equation, was used to calculate B_{11} in those cases where experimental values were not available. Interaction parameters are not very sensitive to errors in the second virial coefficients; for instance, a 20% error in B_{11} causes a difference of 0.01 in the derived χ parameter for n-butanol at 135°C. The interaction parameters at 135°C are given in Table III.

The solubility parameters of the solute probes were calculated by using the Haggenmacher equation and the values of the Antoine equation coefficients, critical constants, and molar volumes obtained from the literature sources mentioned in preceding paragraphs. Experimental data for each polymer were then adjusted to eq. (2) by the least-squares method; δ_2 values were calculated from the slopes, and mean (χ_s/ν_1) values were estimated from the observed slopes and intercepts. The results at 135°C have been summarized in part A of Table IV; α and β coefficients quoted in part B of this table result from the adjustment of the data to the equation

$$\delta_2 = \alpha + \beta t \qquad (7)$$

where t is the temperature (°C). Equation (7) follows from a proposal of Fedors,[45] and provides a rough estimation of the polymer solubility parameter at 25°C. Both the δ_2 standard deviations and the correlation coefficients were included in Table IV to give a better idea of the excellent correlation attained; this simply corroborates the findings of previous papers.[14-19] Experimental results at 135°C and extrapolated values at 25°C have been plotted in Figure 2; there is a regular and almost linear increase in δ_2 with mol % VAc for the copolymers. PVAC, however, has a distinct behavior, as could be predicted from the retention trends discussed in connection with Figure 1.
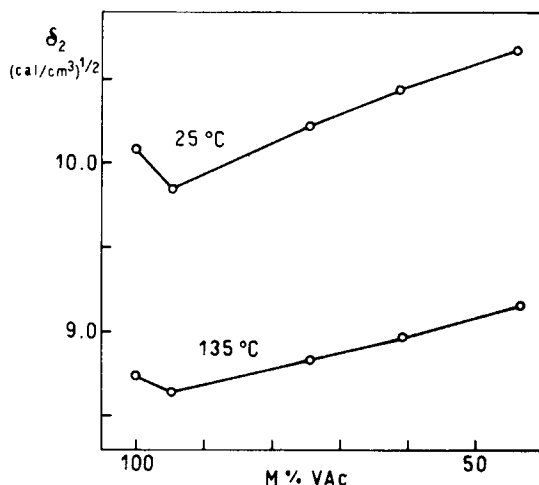
Fig. 2.   Polymer solubility parameter (δ_2) as a function of mol % VAc, at 135 and 25°C.

The choice of the solute probes has apparently no effect on the resulting δ_2: a value of 10.1 $(cal/cm^3)^{0.5}$ at 25°C was obtained both by Guillet and collaborators[14] using 11 hydrocarbons of different types and by Fernández-Berridi et al.[19] employing 13 solutes belonging to very different families, and is coincident with the results arrived at in this paper.

Values of χ_s for each solute–polymer pair at each temperature may be estimated by means of eq. (1), using experimental χ and calculated δ_2 values.
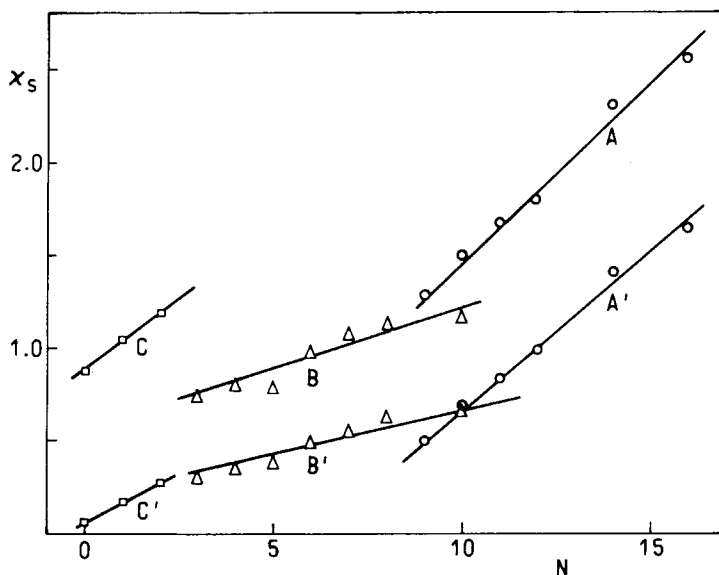

Fig. 3.   Entropy correction term to the interaction parameter (χ_s) against the solute carbon number (N) for several homologous series at 135°C: (A, A′) n-alkanes on 43.4 mol % VAC and PVAc; (B, B′) primary alcohols on 43.4 mol % VAC and PVAc; (C, C′) aromatic hydrocarbons on 43.4 mol % VAc and PVAc.
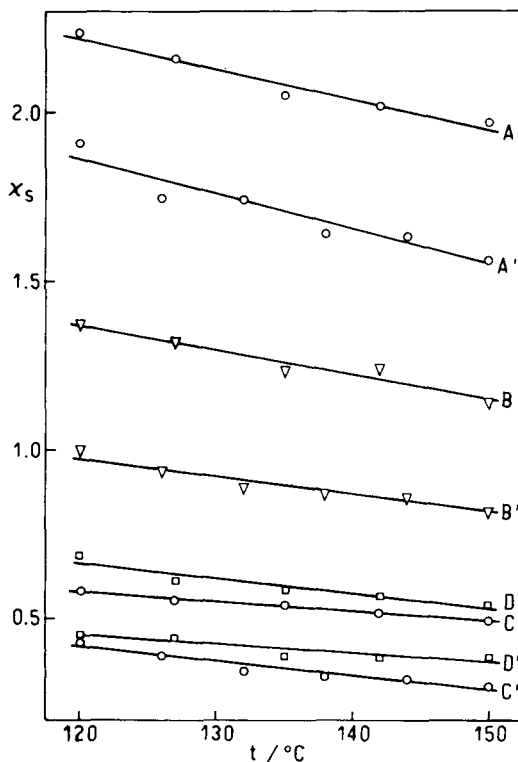
Fig. 4.   Entropy correction term to the interaction parameter (χ_s) against temperature ($^\circ$C) for several representative systems: (A, A') n-hexadecane on 74.4 mol % VAc and PVAc; (B, B') n-undecane on 74.4 mol % VAc and PVAc; (C, C') n-butanol on 74.4 mol % VAc and PVAc; (D, D') benzene on 43.4 mol % VAc and 74.4 mol % VAc.

Such an estimation shows that the χ_s values may fall well outside the 0.3–0.5 range suggested for all systems and temperatures, making an important contribution to χ. Furthermore, χ_s values thus obtained show a regular trend within each homologous series and a good linear relationship exists between χ_s and the temperature, as may be seen in the representative examples plotted in Figures 3 and 4.

Therefore, there is nothing like an universal value of χ_s to be used in the prediction of interaction parameters with moderate accuracy. The prediction improves when mean (χ_s/v_1) quotients, computed *for each polymer* from the slopes and intercepts obtained by applying eq. (2), are used; however, everything seems to point out that the values of these quotients, in contrast to δ_2, shall depend on the choice of the solute probes and their meaning is, at least, doubtful.

There is an apparent discrepancy between the precision of the δ_2 values obtained through eq. (2) and the accuracy of the interaction parameters subsequently estimated with these δ_2 values and eq. (1). The origins have to be sought in the plotting form: since the χ/v_1 term is small in comparison with δ_1^2/RT, the adjustment of the experimental data to eq. (2) overemphasizes the influence of the cohesive energy density terms. This is the reason

SUPPLEMENTARY TABLE I
Specific Retention Volumes (cm^3 g^{-1}) at Several Temperatures
Stationary Phase: PVAC

	120°C	126°C	132°C	138°C	144°C	150°C
n-Nonane	11.46	9.63	9.03	7.47	6.88	6.02
n-Decane	18.88	16.14	14.41	11.66	11.28	9.13
n-Undecane	30.80	25.74	22.96	18.17	16.32	13.84
n-Dodecane	49.76	41.43	35.95	28.07	25.12	2.88
n-Tetradecane	121.2	103.6	81.87	65.58	55.99	46.20
n-Hexadecane	311.7	256.0	197.6	153.4	126.8	105.4
Benzene	18.17	15.63	14.30	13.34	11.01	9.79
Toluene	30.24	25.93	23.14	20.43	16.99	14.84
Ethylbenzene	46.68	39.59	34.90	30.66	24.72	21.45
n-Propanol	25.37	21.21	18.86	15.91	13.39	12.10
n-Butanol	41.60	35.69	30.65	26.25	22.03	19.16
n-Pentanol	70.51	58.95	50.30	41.96	33.35	28.76
n-Hexanol	113.7	99.24	76.70	66.01	53.92	44.25
n-Heptanol	185.7	155.6	120.9	103.3	87.56	65.14
n-Octanol	300.4	248.1	188.6	158.9	133.4	99.72
n-Decanol	770.5	620.7	460.3	374.7	308.9	228.2
Isopropanol	14.71	12.46	11.08	9.99	8.19	7.44
sec-Butanol	25.08	20.74	18.22	15.68	13.36	12.10
tert-Butanol	32.95	28.41	24.13	20.68	17.11	15.20
sec-Pentanol	38.46	32.53	28.89	24.25	20.15	16.80
Cyclohexanol	165.4	144.5	111.7	90.80	76.70	65.52
δ_2(cal/cm^3)$^{1/2}$	8.91	8.86	8.76	8.73	8.60	8.56

SUPPLEMENTARY TABLE II
Specific Retention Volumes (cm^3 g^{-1}) at Several Temperatures
Stationary Phase: 94.8 mol % VAc Copolymer

	120°C	127°C	135°C	142°C	150°C
n-Nonane	11.72	9.84	8.02	6.75	5.52
n-Decane	19.32	16.06	12.93	10.74	8.69
n-Undecane	28.49	23.64	19.05	15.91	13.09
n-Dodecane	48.15	38.85	31.06	25.21	20.39
n-Tetradecane	121.6	95.30	72.48	58.19	45.55
n-Hexadecane	378.7	271.1	201.7	151.9	112.5
Benzene	18.58	14.84	12.52	10.42	8.89
Toluene	28.71	24.05	19.86	16.89	14.16
Ethylbenzene	45.80	37.90	30.70	25.70	21.20
n-Propanol	23.28	18.43	15.18	12.46	10.25
n-Butanol	40.15	33.20	26.72	22.15	18.02
n-Pentanol	68.06	54.78	43.27	35.35	28.36
n-Hexanol	110.2	87.89	67.92	55.18	43.63
n-Heptanol	180.1	140.9	106.6	85.60	66.45
n-Octanol	311.4	238.9	178.2	138.9	102.8
n-Decanol	815.4	603.5	429.6	326.0	244.0
Isopropanol	12.87	10.93	9.15	7.59	6.31
sec-Butanol	22.13	18.62	15.16	12.85	10.67
tert-Butanol	29.57	24.43	19.86	16.66	13.73
sec-Pentanol	22.13	18.62	15.16	12.85	10.67
Cyclohexanol	161.5	128.8	98.97	85.26	66.35
δ_2 (cal/cm^3)$^{1/2}$	8.78	8.70	8.64	8.57	8.43

SUPPLEMENTARY TABLE III
Specific Retention Volumes (cm^3 g^{-1}) at Several Temperatures
Stationary Phase: 74.4 mol % VAC Copolymer

	120°C	127°C	135°C	142°C	150°C
n-Nonane	7.46	6.36	5.38	4.72	4.00
n-Decane	12.34	10.11	8.42	7.16	5.95
n-Undecane	19.44	15.87	12.90	10.81	8.87
n-Dodecane	30.68	24.97	19.74	16.16	13.07
n-Tetradecane	78.36	61.14	46.70	37.55	29.44
n-Hexadecane	201.6	150.5	110.8	85.67	64.86
Benzene	13.47	11.28	9.75	8.43	7.02
Toluene	21.84	18.38	15.18	12.89	10.94
Ethylbenzene	32.48	26.92	21.92	18.42	15.27
n-Propanol	21.57	17.81	14.46	12.14	10.08
n-Butanol	36.15	29.68	23.63	19.54	15.91
n-Pentanol	60.24	48.34	37.70	30.67	24.49
n-Hexanol	96.87	76.46	58.68	47.04	36.97
n-Heptanol	155.8	120.6	90.74	71.59	55.11
n-Octanol	247.4	188.1	139.7	113.4	86.38
n-Decanol	625.4	462.3	332.1	256.1	188.4
Isopropanol	12.67	10.41	9.00	7.66	6.07
sec-Butanol	20.87	17.30	14.02	11.79	9.74
tert-Butanol	27.42	22.61	18.21	15.22	12.47
sec-Pentanol	32.86	26.69	21.25	17.55	14.28
Cyclohexanol	148.6	117.2	90.04	72.17	56.77
δ_2 (cal/cm^3)$^{1/2}$	8.98	8.90	8.83	8.70	8.59

SUPPLEMENTARY TABLE IV
Specific Retention Volumes (cm^3 g^{-1}) at Several Temperatures
Stationary Phase: 60.9 mol % VAc Copolymer

	120°C	127°C	135°C	142°C	150°C
n-Nonane	4.70	4.10	3.51	3.02	2.58
n-Decane	7.56	6.42	5.32	4.55	3.82
n-Undecane	11.80	9.80	7.98	6.67	5.46
n-Dodecane	18.96	15.36	12.12	10.02	7.99
n-Tetradecane	46.12	36.56	27.69	22.14	17.30
n-Hexadecane	120.6	91.54	65.35	50.17	37.58
Benzene	9.22	8.27	6.98	6.09	5.24
Toluene	15.10	12.80	10.67	9.20	7.79
Ethylbenzene	22.08	18.44	15.18	12.83	10.71
n-Propanol	19.42	15.87	12.84	10.65	8.64
n-Butanol	31.49	25.46	20.20	16.66	13.57
n-Pentanol	50.97	40.69	31.61	25.72	20.50
n-Hexanol	80.34	63.35	48.45	38.75	30.35
n-Heptanol	126.4	97.77	73.39	57.67	44.57
n-Octanol	195.8	147.5	108.4	83.93	63.68
n-Decanol	470.7	345.6	245.0	183.5	134.5
Isopropanol	11.01	9.43	7.69	6.50	5.48
sec-Butanol	17.81	14.57	11.77	9.81	8.05
tert-Butanol	23.32	19.07	15.25	12.60	10.29
sec-Pentanol	27.10	21.89	17.43	14.33	11.64
Cyclohexanol	129.7	101.7	77.63	61.91	48.27
δ_2 (cal/cm^3)$^{1/2}$	9.12	9.03	8.96	8.82	8.70

CASTELLS AND MAZZA

SUPPLEMENTARY TABLE V
Specific Retention Volumes (cm^3 g^{-1}) at Several Temperatures
Stationary Phase: 43.4 mol % VAc Copolymer

	120°C	127°C	135°C	142°C	150°C
n-Nonane	3.09	2.71	2.28	1.99	1.66
n-Decane	5.09	4.22	3.46	2.96	2.46
n-Undecane	8.28	6.62	5.22	4.35	3.55
n-Dodecane	13.65	10.76	8.35	6.75	5.33
n-Tetradecane	29.53	22.79	17.51	13.88	10.62
n-Hexadecane	73.71	54.50	38.76	29.45	21.90
Benzene	6.82	5.87	5.15	4.44	3.85
Toluene	10.75	9.16	7.63	6.52	5.59
Ethylbenzene	15.62	13.00	10.68	9.00	7.51
n-Propanol	18.23	15.00	11.89	9.88	8.09
n-Butanol	30.08	23.75	18.56	15.03	11.97
n-Pentanol	47.31	36.99	28.47	22.71	17.84
n-Hexanol	75.44	57.74	42.66	33.71	25.74
n-Heptanol	110.6	83.63	62.51	48.76	37.23
n-Octanol	168.8	130.6	97.25	73.94	55.62
n-Decanol	397.6	293.0	209.6	159.9	113.7
Isopropanol	10.41	8.71	6.94	5.84	4.85
sec-Butanol	15.91	13.27	10.31	8.57	7.02
tert-Butanol	20.94	16.98	13.59	11.14	9.08
sec-Pentanol	24.11	19.63	15.02	12.22	9.76
Cyclohexanol	127.4	96.61	72.78	57.76	44.82
δ_2 (cal/cm^3)$^{1/2}$	9.32	9.25	9.15	9.02	8.91

why points corresponding to excellent solvents for a given polymer fall on the same straight line as those corresponding to poor solvents. These are certainly not novel ideas in polymer solution thermodynamics; they were already advanced by Bristow and Watson in 1958.[9] However, this approach has been applied in many studies during the last years, and it is pertinent to mention its limitations. In spite of these, insofar as easy to apply models of higher accuracy are not available, the solubility parameter remains as a useful guide for suggesting solvents for polymers and gas chromatography as the most straightforward method to measure it.

Supplementary Material. Specific retention volumes at six temperatures in PVAc are given in Supplementary Table I and at five temperatures in the copolymers with 94.8, 74.4, 60.9, and 43.3 mol % VAc in Supplementary Tables II–V.

References

1. D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, *Macromolecules*, 4, 356 (1971).
2. I. Prigogine, *The Molecular Theory of Solutions*, North-Holland, Amsterdam, 1957.
3. P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
4. D. Patterson, *Rubber Chem. Technol.*, **40**, 1 (1967).

5. R. A. Orwoll, *Rubber Chem. Technol.*, **50**, 451 (1977).

6. M. L. Huggins, *Ann. N.Y. Acad. Sci.*, **43**, 1 (1942).

7. R. L. Scott and M. Magat, *J. Polym. Sci.*, **4**, 555 (1949).

8. J. E. Haggenmacher, *Ind. Eng. Chem.*, **40**, 436 (1948).

9. G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).

10. H. Burrel, in *Encyclopedia of Polymer Science and Technology*, Wiley, New York, 1970, Vol. 12, p. 681.

11. M. B. Huglin and D. J. Pass, *J. Appl. Polym. Sci.*, **12**, 473 (1968).

12. R. F. Blanks, *Polym.-Plast. Technol. Eng.*, **8**, 13 (1977).

13. G. Di Paola-Baranyi and J. E. Guillet, *Macromolecules*, **11**, 228 (1978).

14. G. Di Paola-Baranyi, J. E. Guillet, J. Klein, and H. E. Jeberien, *J. Chromatogr.*, **166**, 349 (1978).

15. K. Ito and J. E. Guillet, *Macromolecules*, **12**, 1163 (1979).

16. W. Merk, R. N. Lichtenthaler, and J. M. Prausmitz, *J. Phys. Chem.*, **84**, 1694 (1980).

17. J. E. G. Lipson and J. E. Guillet, *J. Coat. Technol.*, **54**(684), 89 (1982).

18. G. Di Paola-Baranyi, *Macromolecules*, **15**, 622 (1982).

19. M. J. Fernández-Berridi, G. M. Guzmán, J. M. Elorza, and L. Garijo, *Eur. Polym. J.*, **19**, 445 (1983).

20. M. K. Lindemann, in *Encyclopedia of Polymer Science and Technology*, Wiley, New York, 1971, Vol. 15, p. 618.

21. D. D. Deshpande and O. S. Tyagi, *Macromolecules*, **11**, 746 (1978).

22. R. K. Tubbs and T. K. Wu, in *Polyvinyl Alcohol. Properties and Applications*, C. A. Finch, Ed., Wiley, New York, 1973, Chap. 8.

23. R. K. Tubbs, *J. Polym. Sci.*, A-1, **4**, 623 (1966).

24. I. Ahmed and J. G. Pritchard, *Polymer*, **20**, 1492 (1979).

25. D. Braun, H. Cherdron, and W. Kern, *Praktikum der Makromolekularen Organischen Chemie*, 3rd. ed., Huthig Verlag, Heidelberg, 1979, p. 308.

26. E. Nagai and W. Sagane, *Kobunshi Kagaku*, **12**, 195 (1955).

27. D. E. Martire and P. Riedl, *J. Phys. Chem.*, **72**, 3478 (1968).

28. A. B. Littlewood, C. S. G. Phillips, and D. T. Price, *J. Chem. Soc.*, 1480, (1955).

29. J. R. Conder, J. G. Rees, and S. McHale, *J. Chromatogr.*, **258**, 1 (1983).

30. D. R. Fritz and E. Sz. Kováts, *Anal. Chem.*, **45**, 1175 (1973).

31. D. E. Martire, *Anal. Chem.*, **46**, 626 (1974).

32. Ref. 20, p. 632.

33. R. R. Dreisbach, *Adv. Chem. Ser.* 1955, No. 15, 1959, No. 22, 1961, No. 29.

34. J. A. Riddick and W. B. Bunger, *Organic Solvents*, 3rd. ed., Wiley-Interscience, New York, 1970.

35. T. E. Jordan, *Vapor Pressure of Organic Compounds*, Interscience, New York, 1954.

36. C. F. Spencer and S. E. Adler, *J. Chem. Eng. Data*, **23**, 83 (1978).

37. K. M. Watson, *Ind. Eng. Chem.*, **35**, 398 (1984).

38. M. L. McGlashan and J. B. Potter, *Proc. Roy. Soc. A*, **267**, 478 (1962).

39. A. P. Kudchadker, G. H. Alani, and B. J. Zwolinski, *Chem. Rev.*, **68**, 659 (1968).

40. E. A. Guggenheim and C. J. Wormald, *J. Chem. Phys.*, **42**, 3775 (1965).

41. J. D. Lambert, *Disc. Faraday Soc.*, **15**, 226 (1953).

42. C. Black, *Ind. Eng. Chem.*, **50**, 391 (1958).

43. J. P. O'Connell and J. M. Prausnitz, *Ind. Eng. Chem., Proc. Des. Dev.*, **6**, 245 (1967).

44. J. D. Dymond and E. B. Smith *The Virial Coefficients of Pure Gases and Mixtures*, Claredon, Oxford, 1980.

45. R. F. Fedors, *Polym. Eng. Sci.*, **14**, 147 (1974).