

Gas–Liquid Chromatographic Study of the Solution Thermodynamics of Hydroxylic Derivatives in Selected Polymeric Liquids

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Applications of gas chromatography have been enhanced through conversion of many chemical compounds to derivatives with suitable reagents. This study measured retention volumes of a number of hydroxylic derivatives in polymeric stationary phases. A number of alkanes and aromatics were included in the study for comparison with the derivatives. The stationary phases include a poly(dimethylsiloxane), a poly(methylphenylsiloxane), a poly[methyl(trifluoropropyl)siloxane], and a methoxy poly(ethylene oxide). The selected derivatives were acetates, trimethylsilyl ethers, trifluoroacetates, and pentafluoropropionates. The hydroxylic compounds included butyl alcohol, cyclohexanol, and *m*- and *p*-methylphenols; *n*-butyl *tert*-butyl ether was included for comparison with *n*-butyl trimethylsilyl ether. The effects of derivatizing groups on the interaction parameter were considered as a summation of hydrocarbon core and derivative groups. Linear free energy relationships were identified for *n*-alkanes, aromatics, and *n*-butyl derivatives. Some thermodynamic results could be interpreted in terms of molecular structure of molecules and specific solute–solvent interactions. Results here support an approach to selecting derivatives for separations matched to column liquid phases.

1. Introduction

Gas–liquid chromatography (GLC) has been used for many years as an effective technique for obtaining solubility data^{1–4} and other physicochemical information^{5–9} for solute vapors in polymeric materials, particularly at infinite dilution. Most studies to date have focused on solutes that are similar to the monomer or the structural units of polymers, such as alkanes, aromatics, and oxygenated or chlorinated compounds. These solutes generally have been linear, nonpolar, or slightly polar, and their solution properties were explained in terms of dispersion forces and dipole and hydrogen bonding interactions. Fluorinated compounds were not generally studied despite their applications in derivatization in gas chromatography. Derivatization of certain functional groups is frequently used in gas chromatographic studies for increasing volatility, enhancing isomer separations, and imparting thermal stability to analytes.^{10,11} In our previous study on these derivatives, it was noted that many consisted of two parts with dissimilar properties so-called “dual character” molecules.¹²

Here, we extend the use of gas chromatography to solutes in Dow corning (DC) polymeric silicone type solvents to study some common derivatives of alcohols and phenols for which vapor pressure data are available, together with some aliphatic and aromatic hydrocarbons for comparison. The polymeric solvents or stationary phases used here include a poly(dimethylsiloxane) (DC-200), a poly(methylphenylsiloxane) (DC-550), and a poly[methyl(trifluoropropyl)siloxane] (QF-1) as well as a methoxy ether of a poly(ethylene oxide) (PEO). QF-1 is unique in that it contains some fluorocarbon units; PEO solvent is used

for comparison with the silicones. The properties and effects of using various derivatizing agents can be examined as was done earlier with low molecular weight stationary phases.¹² There is also an opportunity for obtaining additional data to which solution thermodynamic theory might be applied. The chosen representative derivatives were acetates, trimethylsilyl ethers (TMSE), trifluoroacetates (TFA), and pentafluoropropionates (PFP) of the following solutes: *n*-butyl alcohol (aliphatic), cyclohexanol (naphthenic), and *m*- and *p*-methylphenols (aromatic). *n*-Butyl *tert*-butyl ether was included for comparison with the trimethylsilyl ether of *tert*-butyl alcohol. The solution data for these compounds in several polymers that contain substitution groups similar to some of the derivatizing groups facilitate a crossed comparison of thermodynamic properties of both solutes and solvents.

Solution thermodynamic properties have been found to depend on the geometry of solutes even when there is no known specific interaction between solutes and solvents, such as in alkane systems.^{13–19} This results from altered solvent structure by a solute with different geometry so that an orientation enthalpy and entropy are observed for the solution process.¹³ Effects were invoked in a study of second-order model parameters, which permit distinction between isomers.¹⁹ This geometry and isomer effect will be even more pronounced when an asymmetric interaction force accompanies geometric differences. The orientation effect accompanying an interaction force field can be more readily observed when a molecule can rotate to facilitate preferential interaction between solute and solvent. This type of molecule should have a globular structure, but with different properties at two loci, so that a net interaction effect would be observed without being confounded from such solvent structure change effects due to solute molecule geometry.

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Molecules with such ideal structures are not available to us. However, a number of the derivatives with “dual character”¹² were selected for their related characteristics. Such molecules might be expected to assume preferential orientation and contact with different structural units of liquid phases to affect solution thermodynamic properties.

Because of their importance, significant efforts have been devoted to designing liquid phases suited to separating aromatic meta and para isomers.^{20,21} Further study of the orientation effects resulting from formation of various derivatives should contribute to the understanding of the separation mechanisms and solvent selectivity and possibly assist in future molecular design efforts.

2. Theory

When an infinitesimal amount of solute sample is introduced into a GLC column with a polymeric stationary phase, the specific retention volume of the solute at the column temperature, V_g^T , can be related to the Flory–Huggins interaction parameter, χ , by^{1–3,12,22,23}

$$\chi = \ln \frac{RT}{V_2^0 P_2^0 V_g^T \rho_s} + \frac{1}{m} - 1 + \frac{P_2^0}{RT} (B_{22} - V_2^0) - \frac{P_o J}{RT} (2B_{23} - \bar{V}_2^\infty) \quad (1)$$

where a pressure correction

$$J = \frac{3}{4} \left[\frac{(P_i/P_o)^4 - 1}{(P_i/P_o)^3 - 1} \right]$$

P_2^0 , V_2^0 , and B_{22} are the vapor pressure, liquid molar volume, and the second virial coefficient of the solute, respectively, and ρ_s is the density of the polymer. B_{23} is the crossed second virial coefficient between solute vapor and the carrier gas. \bar{V}_2^∞ is the partial molar volume of the solute in the stationary phase at infinite dilution. Usually this does not differ from V_2^0 by more than 5%; therefore, it may be replaced by V_2^0 . P_i and P_o are column inlet and outlet pressures, respectively. The molar volume ratio term, $1/m$, of eq 1 becomes negligible when a high molecular weight solvent is used. The last term in eq 1 has been overlooked frequently. Unfortunately, it can be neglected only when using helium carrier gas, since B_{23} is positive and cancels most of the positive solute molar volume, \bar{V}_2^∞ . Conder and Langer²⁴ noted earlier that an increase of 1–2% in the retention volumes of hydrocarbons could be observed when helium gas is used instead of nitrogen.

The second virial coefficients of solutes were calculated here with the equation of McGlashan et al.^{25,26}

$$\frac{B_{22}}{V_c} = 0.43 - 0.886 \left(\frac{T_c}{T} \right) - 0.694 \left(\frac{T_c}{T} \right)^2 - 0.0375 (n - 1) \left(\frac{T_c}{T} \right)^{4.5} \quad (2)$$

where critical volume, V_c , critical temperature, T_c , and the carbon number, n , are crucial parameters. For compounds other than normal alkanes, Guggenheim and Wormald²⁷ have suggested using a “pseudo” carbon number obtained from liquid vapor pressures as the effective carbon number. Equation 2 and the following combination rules are used for computing the cross

second virial coefficient, B_{23}

$$T_{c,23} = (T_{c,2} T_{c,3})^{1/2} \quad (3)$$

$$V_{c,23} = (V_{c,2}^{1/3} + V_{c,3}^{1/3})^3 \quad (4)$$

$$n_{23} = (n_2 + n_3)/2 \quad (5)$$

where subscripts 2 and 3 refer to the solute vapor and carrier gas, respectively. For permanent carrier gases, such as helium and nitrogen, the effective carbon number is unity, according to McGlashan et al.^{25,26} In the original Flory–Huggins treatment, the interaction parameter, χ , was a constant contact energy term. However, experience has shown that χ usually depends on temperature and concentration.^{28,29} Guggenheim³⁰ suggested that χ , the free energy of contact, be separated so that

$$\chi = \chi_H + \chi_S \quad (6)$$

Where the reduced excess enthalpy of solution, χ_H , and reduced residual entropy of solution, χ_S , are defined as

$$\chi_H = -T \left(\frac{\partial \chi}{\partial T} \right) = \Delta \bar{H}_e^\infty / RT \quad (7)$$

$$\chi_S = \frac{\partial(T\chi)}{\partial T} = -\Delta \bar{S}_{re}^\infty / R \quad (8)$$

Here $\Delta \bar{S}_{re}^\infty$ is the residual entropy of solution or the non-combinatorial part of the entropy of solution. It is associated with solute–solvent interaction. The residual enthalpy is generally considered to be the excess enthalpy of solution.

3. Experimental Section

The GLC equipment used for this study has been described earlier.¹² Helium was used as the carrier gas. Flow rates were kept at about 40 mL/min and were measured using a soap bubble flow meter. Decreasing the flow rate did not show detectable change in the corrected retention volume. Measurements were made at 80 and 100 °C.

All stationary phase solvents (Anspec Company) were used as purchased. Carbowax 750, a methoxy poly(ethylene oxide), has Mn of ca. 750 as reported by the manufacturer. The molecular weights, measured by vapor pressure osmometry, for the poly(phenylmethylsiloxane) (DC-550) and poly[methyl-(trifluoropropyl) siloxane] (QF-1) were 1 722 and 13 050, respectively. The poly(dimethylsiloxane) fluid (DC-200) had an average molecular weight of 30 400 based on a membrane osmometry measurement. All molecular-weight measurements were made by ArRo Laboratory (Joliet, Illinois). The molecular-weight dispersion is not known. Commercially unavailable solutes were synthesized and have been reported earlier with their vapor pressures.¹⁰ A 100/120 mesh silanized fire-brick (Gas–Chrom RZ from Anspec) was the solid support for all liquid phases except for QF-1. Inert 60/80 mesh silanized Celite (Gas–Chrom Q from Anspec) was used for QF-1.

4. Results

Specific retention volumes per gram of stationary phases, V_g^T , at 80 and 100 °C are shown in Table 1. The Flory–Huggins interaction parameters at 80 and 100 °C were calculated and listed in Table 2. The required critical temperatures and volumes were taken from standard sources³¹ or calculated using a group

TABLE 1: Specific Retention Volumes (V_g^T)^a for Polymeric Stationary Phases at 80 and 100 °C (in cm³/gm)

solutes	DC-200		DC-550		QF-1		PEO	
	80 °C	100 °C	80 °C	100 °C	80 °C	100 °C	80 °C	100 °C
<i>n</i> -heptane	94.4	55.0	76.5	44.9	22.4	13.6	19.0	12.8
<i>n</i> -octane	196.2	105.9	164.2	89.6	42.2	24.0	36.3	23.0
<i>n</i> -nonane	405.4	202.5	349.3	176.7	77.3	41.8	69.1	41.2
benzene	69.9	43.0	86.9	52.1	37.9	23.4	96.9	57.8
toluene	148.5	84.9	190.8	106.5	74.2	42.4	182.0	102.7
<i>o</i> -xylene	361.9	189.7	500.8	255.6	172.9	91.6	444.9	232.3
1-methyl-3-ethylbenzene	584.7	289.8	803.9	388.1	224.1	114.1	573.1	289.7
<i>n</i> -butyl acetate	232.9	122.5	298.8	148.9	178.8	91.4	240.7	127.0
cyclohexyl acetate	1130.0	517.0	1736.9	761.7	773.0	352.4	1320.8	613.4
<i>m</i> -tolyl acetate	2382.6	1013.4	<i>b</i>	1944.8	3166.8	1227.5	<i>b</i>	4182.0
<i>p</i> -tolyl acetate	2466.0	1040.1	<i>b</i>	2005.7	3315.0	1291.0	<i>b</i>	4375.0
<i>n</i> -butyl TMSE	199.2	104.5	172.6	91.3	50.1	27.4	45.7	27.5
cyclohexyl TMSE	850.0	408.2	877.7	412.6	193.8	98.0	216.3	115.5
<i>m</i> -tolyl TMSE	2128.0	899.0	<i>b</i>	1189.9	808.7	351.5	1650.0	735.2
<i>p</i> -tolyl TMSE	2272.0	957.2	<i>b</i>	1283.5	833.1	361.9	1798.0	797.0
<i>n</i> -butyl TFA	72.9	42.1	75.2	42.0	80.1	43.3	44.5	25.9
cyclohexyl TFA	336.1	183.5	448.5	217.4	333.2	163.7	211.4	111.4
<i>m</i> -tolyl TFA	580.5	276.0	753.7	345.1	612.3	272.8	826.2	367.2
<i>p</i> -tolyl TFA	615.0	289.8	800.3	363.1	641.7	285.7	898.0	394.6
<i>n</i> -butyl PFP	93.3	51.5	85.0	46.0	95.3	50.4	36.9	21.5
cyclohexyl PFP	445.2	218.4	484.9	231.0	385.7	182.8	168.1	89.0
<i>m</i> -tolyl PFP	712.3	325.8	804.5	359.3	713.5	305.0	590.2	265.3
<i>p</i> -tolyl PFP	753.1	345.5	853.1	381.0	744.7	320.2	628.8	283.7
<i>n</i> -butyl <i>tert</i> -butyl ether	203.2	107.9	196.7	102.5	55.0	31.0	60.3	35.8

^a V_g^T is the corrected retention volume per gram of liquid phase at the indicated temperature. ^b Retention volumes were very large and hence not measured.

TABLE 2: Interaction Parameter (χ) at 80 and 100 °C for Solutes in Polymeric Stationary Phases

solutes	DC-200		DC-550		QF-1		PEO	
	80 °C	100 °C	80 °C	100 °C	80 °C	100 °C	80 °C	100 °C
<i>n</i> -heptane	0.345	0.310	0.553	0.527	1.505	1.444	2.037	1.873
<i>n</i> -octane	0.389	0.373	0.580	0.546	1.653	1.578	2.192	2.010
<i>n</i> -nonane	0.443	0.420	0.612	0.572	1.828	1.721	2.349	2.145
benzene	0.574	0.553	0.323	0.319	0.873	0.875	0.254	0.253
toluene	0.598	0.564	0.317	0.310	1.005	0.979	0.418	0.399
<i>o</i> -xylene	0.693	0.664	0.350	0.341	1.151	1.106	0.533	0.501
1-methyl-3-ethylbenzene	0.672	0.647	0.349	0.342	1.354	1.297	0.769	0.715
<i>n</i> -butyl acetate	0.482	0.452	0.225	0.248	0.470	0.469	0.518	0.483
cyclohexyl acetate	0.574	0.556	0.144	0.159	0.678	0.655	0.506	0.463
<i>m</i> -tolyl acetate	1.513	1.410	—	0.75	0.952	0.936	—	0.068
<i>p</i> -tolyl acetate	1.504	1.404	—	0.739	0.929	0.905	—	0.043
<i>n</i> -butyl TMSE	0.233	0.236	0.401	0.393	1.340	1.292	1.857	1.720
cyclohexyl TMSE	0.316	0.276	0.313	0.293	1.519	1.426	1.851	1.703
<i>m</i> -tolyl TMSE	0.554	0.564	—	0.308	1.249	1.225	0.968	0.921
<i>p</i> -tolyl TMSE	0.537	0.547	—	0.278	1.269	1.243	0.932	0.886
<i>n</i> -butyl TFA	0.793	0.721	0.769	0.725	0.426	0.411	1.329	1.306
cyclohexyl TFA	0.666	0.548	0.392	0.387	0.400	0.382	1.254	1.166
<i>m</i> -tolyl TFA	0.982	0.907	0.728	0.688	0.650	0.639	0.742	0.732
<i>p</i> -tolyl TFA	1.006	0.936	0.755	0.714	0.691	0.669	0.746	0.736
<i>n</i> -butyl PFP	0.777	0.731	0.895	0.861	0.484	0.473	1.765	1.746
cyclohexyl PFP	0.673	0.597	0.615	0.567	0.543	0.499	1.807	1.654
<i>m</i> -tolyl PFP	0.895	0.833	0.801	0.762	0.619	0.625	1.241	1.196
<i>p</i> -tolyl PFP	0.871	0.805	0.771	0.729	0.606	0.601	1.218	1.156
<i>n</i> -butyl <i>tert</i> -butyl ether	0.310	0.304	0.356	0.364	1.342	1.272	1.649	1.526

contribution method.³² Densities of solutes and solvents have been reported earlier.³³

Poly(dimethylsiloxane)s (PDMS) have been the subject of many studies.^{34–51} Although these stationary phases can be used at higher temperatures,⁷ most PDMS studies have been conducted at temperature ranges below this study. A wide temperature range measurement for PDMS was made by Galin.³⁴ His retention volumes are presented as V_g^0 values. When converted to V_g^T , a value of 88.6 cm³/g at 80 °C and a value of 50.5 cm³/g at 100 °C were calculated for *n*-heptane. Parcher et al.⁴⁶ measured specific retention volumes for phenyl–methyl silicones with different degrees of phenyl substitution on the silicones. The polymer sample with zero phenyl group concen-

tration is essentially PDMS. Their V_g^T values at 100 °C for *n*-heptane and benzene are 52.5 and 39.7 cm³/g, respectively. The retention volumes for *n*-heptane are higher than those obtained by Galin but still lower than ours. Roth and Novák⁴² conducted measurement of alkanes in PDMS and compared results of several studies. The V_g^0 of *n*-octane at 80 °C ranged from 143.8 to 147.6 cm³/g for low and medium molecular weight PDMS. This compares well with the 151.8 cm³/g of this study. More recently Humpa et al.⁴⁷ measured the interaction parameter of several alkanes in several poly(phenylmethylsiloxane)s. Their result for *n*-octane in DC-550 at 80 °C was 159 cm³/gm when converted to V_g^T . This was reasonably close to our value of 164 cm³/gm. Retention volumes and interaction

parameters are known to depend on the molecular weight of stationary phases,^{52–54} which might explain some difference between this study and literature results. The use of helium as a carrier gas produces a slightly higher retention volume and lower χ value as noted earlier.²⁴

PEO has also been the subject of several studies^{53–62} but the molecular weights of the polymers used were generally higher than with this study. Wide temperature range static measurements of sorption of benzene by PEO were made by Saeki and Bonner.⁵⁴ The Flory–Huggins interaction parameters were extrapolated to zero benzene concentration and plotted vs temperature. They found that a molecular weight dependent minimum occurred around 80 °C. At temperatures higher than 90 °C, the χ value becomes constant and falls within a range of 0.22–0.3, depending on the polymer molecular weight. Galin⁵³ compared several values for PEO in his GLC study using a PEO with $M_n = 10\,000$. His χ value for *n*-heptane at 70 °C was 1.93, which is reasonably close to our value at 80 °C, 2.04. The small difference is probably the effect of the low molecular weight of the Carbowax sample used here (750 vs 10 000) and possibly the methoxy terminal group. The specific retention volumes of selected solutes in PEO were shown to increase as molecular weights decreased.⁵⁹ The calculation of the interaction parameter was also affected by the molecular weight of polymer through the molar volume ratio, $1/m$, in eq 1, which will produce an important difference with Carbowax 750 because of the low molecular weight.

There were fewer studies with poly[methyl(trifluoropropyl)siloxanes] than with other polymers.^{63–65} Roth⁶³ reported the results of QF-1 as weight fraction activity coefficient. When converting to χ , the value of *n*-octane at 80 °C was about 1.55, which was close to our 1.65 value. Becerra et al.⁶⁴ studied QF-1 and another commercial grade of poly[methyl(trifluoropropyl)siloxane], OV-215. They reported χ values of *n*-octane to be 1.55 and 1.37 at 90 and 120 °C, respectively. These values also were close to those of this work as well as Roth.

5. Discussion

5.1. Retention Volumes and Activity Coefficients. The effect of derivatizing groups on retention behavior can be seen by comparing specific retention volumes of solutes in different solvents. A homologous series of solutes generally falls on a straight line when the $\log V_g^T$ for a solvent pair are plotted against each other.^{12,22,23} This is a convenient method for comparing and scanning interaction between solutes and solvents, particularly in the presence of a specific interaction and when the solvent molecular weights or the vapor pressure of solutes are unknown.

The $\log V_g^{100}$ values for DC-200 and DC-550 are plotted in Figure 1. These two solvents differ from each other by some silicone substituents in the siloxane chain. DC-200, a PDMS fluid, contains all methyl groups, while DC-550 is a copolymer of dimethylsilyl and methylphenyl groups in a silicone polymer.^{10,47} As a result, aromatics tend to be somewhat retained by DC-550 and alkanes tend to be retained somewhat more by DC-200. However, the distance between the alkane and aromatic lines is small, indicating only a small difference between the solvating power of the two polymers. Most derivatives fall between the limits formed by alkanes and aromatic solute plots. Notable exceptions are for the two tolyl acetates. Both tolyl and acetate groups favor DC-550, which leads to higher retention volumes in DC-550. The effects of fluorine substituents in TFA derivatives can be seen from the large decrease of retention volumes compared to the acetates for all hydroxylic parent

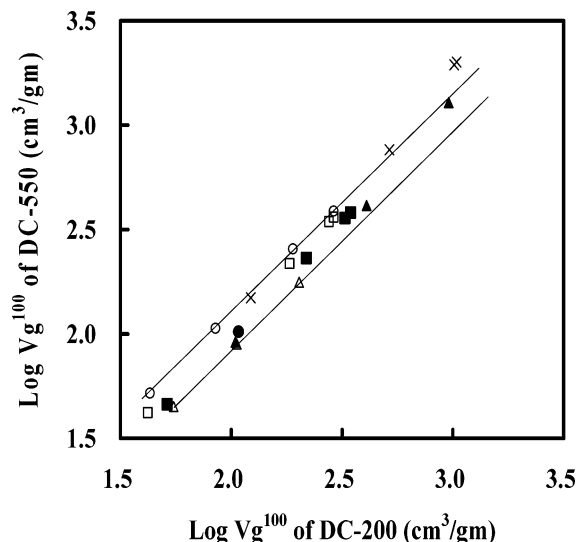


Figure 1. Log–log plot of V_g^{100} for solutes of this study eluted from poly(dimethyl) siloxane (DC-200) and poly(phenylmethyl) siloxane (DC-550). (Δ) *n*-Alkanes; (\circ) aromatics; (\times) acetates; (\blacktriangle) trimethylsilyl ethers; (\square) trifluoroacetates; (\blacksquare) pentafluoropropionates; (\bullet) *n*-butyl-*tert*-butyl ether. Lines are drawn to show linearity for aromatic and alkane series.

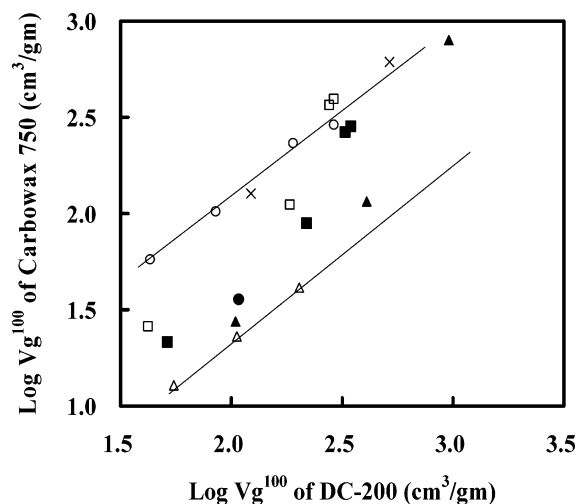


Figure 2. Log–log plot of V_g^{100} for solutes of this study eluted from poly(dimethyl) siloxane (DC-200) and poly(ethylene oxide) (Carbowax 750). (Δ) *n*-Alkanes; (\circ) aromatics; (\times) acetates; (\blacktriangle) trimethylsilyl ethers; (\square) trifluoroacetates; (\blacksquare) pentafluoropropionates; (\bullet) *n*-butyl-*tert*-butyl ether. Lines are drawn to show linearity for aromatic and alkane series.

compounds in DC-200 and DC-550. This effect might be explained as the results of higher vapor pressure and higher interaction parameter caused by shielding of ester group by fluorocarbon and unfavorable fluorocarbon–hydrocarbon contacts in solution. Furthermore, the effect of fluorocarbon is essentially saturated by the first fluoromethylene unit and the additional fluoromethylene unit from PFP's result in only a small change in interaction parameters. In fact, the retention volumes of PFP's increase slightly in DC-200 and DC-550 as a consequence of higher molecular weight and lower vapor pressure.

In Figure 2, the retention volumes with PEO (Carbowax 750) are plotted vs DC-200. PEO tends to introduce strong polar–aromatic interactions, which results in an increase in the retention volumes of tolyl acetates and other aromatic derivatives. Even with strong interactions involved, the relative positions of retention data are still retained, e.g., TFAs are lower

TABLE 3: Free-Volume Effects, χ_{FV}^* , of Solutes in Four Liquid Phases for 80 and 100 °C

solutes	DC-200		DC-550		QF-1		PEO	
	80 °C	100 °C	80 °C	100 °C	80 °C	100 °C	80 °C	100 °C
<i>n</i> -heptane	0.111	0.146	0.301	0.400	0.268	0.363	0.486	0.605
<i>n</i> -octane	0.079	0.109	0.258	0.355	0.226	0.318	0.443	0.561
<i>n</i> -nonane	0.058	0.085	0.230	0.326	0.199	0.289	0.416	0.536
benzene	0.075	0.099	0.206	0.274	0.183	0.249	0.333	0.415
toluene	0.039	0.056	0.148	0.208	0.128	0.185	0.265	0.340
<i>o</i> -xylene	0.012	0.022	0.094	0.144	0.077	0.124	0.196	0.263
1-methyl-3-ethylbenzene	0.022	0.037	0.129	0.191	0.108	0.167	0.254	0.336
<i>n</i> -butyl acetate	0.044	0.064	0.168	0.237	0.146	0.210	0.301	0.386
cyclohexyl acetate	0.011	0.022	0.104	0.163	0.085	0.139	0.224	0.303
<i>m</i> -tolyl acetate	0.000	0.001	0.051	0.097	0.037	0.077	0.151	0.221
<i>p</i> -tolyl acetate	0.000	0.003	0.061	0.111	0.046	0.090	0.168	0.242
<i>n</i> -butyl TMSE	0.067	0.091	0.209	0.286	0.184	0.257	0.354	0.448
cyclohexyl TMSE	0.023	0.038	0.134	0.199	0.112	0.173	0.265	0.351
<i>m</i> -tolyl TMSE	0.012	0.024	0.110	0.172	0.090	0.147	0.237	0.321
<i>p</i> -tolyl TMSE	0.005	0.013	0.086	0.140	0.068	0.118	0.200	0.276
<i>n</i> -butyl TFA	0.126	0.160	0.304	0.397	0.274	0.363	0.473	0.582
cyclohexyl TFA	0.049	0.070	0.184	0.259	0.159	0.230	0.329	0.422
<i>m</i> -tolyl TFA	0.033	0.052	0.163	0.237	0.138	0.208	0.310	0.405
<i>p</i> -tolyl TFA	0.033	0.053	0.164	0.238	0.139	0.209	0.312	0.407
<i>n</i> -butyl PFP	0.110	0.143	0.282	0.372	0.253	0.339	0.447	0.554
cyclohexyl PFP	0.054	0.078	0.203	0.285	0.176	0.253	0.361	0.464
<i>m</i> -tolyl PFP	0.040	0.061	0.176	0.253	0.151	0.223	0.326	0.424
<i>p</i> -tolyl PFP	0.043	0.065	0.185	0.265	0.159	0.234	0.341	0.442
<i>n</i> -butyl <i>tert</i> -butyl ether	0.054	0.076	0.184	0.255	0.161	0.228	0.320	0.408

in DC-200 and higher in PEO than PFPs. The spread between TFAs and PFPs reflects the contribution to the retention volume of an additional fluoromethylene unit. This quantity is approximately constant for the four types of parent hydroxyl compounds examined, which indicates a constant effect on vapor pressure and interaction parameters from a fluoromethylene group addition. By contrast, addition of a methylene unit in alkanes and aromatics generally gives a greater retention volume change than does a fluoromethylene unit. For a methylene unit addition in the solute, the incremental retention volume tends to be slightly higher for aromatics than with *n*-alkanes. Most of these differences originated from vapor pressure differences. For an incremental carbon atom, the vapor pressure decreased by a ratio of about 1.3, 2.3, and 2.8 for fluoroderivative, *n*-alkanes, and aromatics, respectively.¹²

5.2. Free-Volume Effect. GLC systems generally involve volatile solutes and a condensed nonvolatile solvent. The free-volume effect can be important with polymer solutions because the free volumes of volatile, small solute molecules are substantially different from nonvolatile condensed polymeric phases. Flory et al.⁶⁷ derived an equation which makes it possible to treat the free volume contribution to the excess free energy of mixing. With the equations of Flory et al., a different interaction parameter χ^* can be obtained through eq 1 using core volumes of solutes and solvents in the first two terms of the right-hand side of eq 1.^{1-3,66} This interaction parameter has two components

$$\chi^* = \chi_{\text{FV}}^* + X_{12} \frac{V_2^*}{\tilde{V}_1} \quad (9)$$

where subscripts 1 and 2 refer to the polymer and solute, respectively. χ_{FV}^* is the free-volume effect defined as^{29,67}

$$\chi_{\text{FV}}^* = \frac{P_2^* V_2^*}{RT} \left[3\tilde{T}_2 \ln \left(\frac{\tilde{V}_2^{1/3} - 1}{\tilde{V}_1^{1/3} - 1} \right) + \frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}_1} \right] \quad (10)$$

Where $\tilde{V} = V/V^*$, $\tilde{T} = T/T^*$, and P^* , V^* , and T^* are characteristic parameters. The last term of eq 9 takes into account the contact energy differences between solutes and solvents.

P^* , V^* , and T^* of hydrocarbons were calculated from the equations of Flory et al.,⁶⁷ using data from Allen et al.⁶⁸ For derivatives, the required density data for solute and solvents were measured in our laboratories.^{10,33} For derivatives for which compressibility information are not available, the relation proposed by Biroš et al.⁶⁹ might be used

$$P^* = (\delta \tilde{V})^2 \quad (11)$$

where δ is the solubility parameter and \tilde{V} is the reduced volume of solutes. The values of χ_{FV}^* for solutes used here were calculated and are listed in Table 3. All free-volume contributions increase with rising temperature. Thus, an expanded solute gives a higher free volume effect. Equation 10 also indicates that for any given solute a larger free-volume contribution will be found in a more condensed solvent. PEO is the most condensed solvent here and would give the largest χ_{FV}^* . The free volume effect is not always negligible. Flory suggested that a χ value of 0.5 can be used as a criterion for phase separation of polymer solutions.²⁸ The χ_{FV}^* of several solutes in PEO exceeds this limit at 100 °C. Although other effects, e.g., contact energy differences, can be larger than the free-volume effects, the free-volume effect alone can cause phase separation for *n*-hexane—polyethylene solutions,⁷⁰ in which structural units are similar. Because they incorporate the free-volume contribution, the values of χ do not exclusively represent a contact energy difference between solutes and solvents. However, a comparison of relative values of χ for two solutes in the same solvent, as shown below for derivatives, can eliminate the major portion of free volume effects.

5.3. Effects of Groups on Interaction Parameters. The effect of derivatizing groups on solute volatility depends on the product of vapor pressure and the interaction parameter (see eq 1). The effect of derivatizing agents on the vapor pressure alone has been discussed.¹² The effects of derivatizing agents on χ can be obtained by considering solute molecules as a combination of different moieties. The use of the group contribution method to calculate activity coefficients of solutes has a long history.^{32,71,72} Most studies try to separate molecules to the most basic structural units. Here a different approach is used because our main objective is to compare the effect of derivatives. A

TABLE 4: Effect of Hydrocarbon Cores and Derivatizing Groups on the Interaction Parameter (χ) at 100 °C

	DC-200	DC-550	QF-1	PEO
<i>n</i> -Butyl	0.189	0.282	0.810	1.049
Cyclohexyl	0.139	0.076	0.893	1.001
<i>m</i> -Phenyl	0.589	0.214	1.108	0.386
<i>p</i> -Phenyl	0.588	0.212	1.088	0.361
Acetate	0.655	0.016	-0.213	-0.533
TMSE	0.052	0.171	0.292	0.654
TFA	0.442	0.449	-0.442	0.309
PFP	0.395	0.554	-0.410	0.773
<i>tert</i> -butoxyl	0.117	0.078	0.496	0.537

molecule is divided into two parts with a hydrocarbon core and a derivative group. The χ value of the first hydrocarbon core is determined from three *n*-alkanes used. Since interaction parameters are linear with respect to carbon number, the linear regression result for octane was considered as twice of the *n*-butyl group. Other hydrocarbon cores were calculated based on the difference of χ values relative to *n*-butyl groups. For example, the difference between four *n*-butyl derivatives and cyclohexyl derivatives were averaged, and from this value, the χ value of the cyclohexyl core was determined. After hydrocarbon cores were determined, the χ values of derivatizing groups were calculated from solutes with the same derivative by subtracting the contribution of hydrocarbon cores. For most derivatives, the averages were taken using four hydroxyl compounds. The effect of the *tert*-butoxyl group was determined from the difference of χ between *n*-butyl *tert*-butyl ether and the *n*-butyl group.

The effects of hydrocarbon cores and derivatizing groups on χ values at 100 °C are shown in Table 4. The values of cyclohexyl and *n*-butyl groups are similar because they have similar size. The difference between *m*- and *p*-phenyl groups is also small. But the difference is higher in QF-1 and PEO. This indicates that these two solvents may be more isomer selective than the other two solvents. In DC-200, acetates had higher interaction parameters than TFA and PFP. The fluoroesters were more favorable in the PDMS solvent than acetates. In DC-550, the situation was reversed; acetates now interact more favorably

with phenyl groups in DC-550 than do fluoroesters. Fluorine-containing QF-1 gave a larger decrease in the interaction parameter for esters, and the difference between esters and ethers was also significant. QF-1 is known to interact with ester groups.⁶⁵ This was true with acetates and even stronger with TFA and PFP. This can be explained by the favorable interaction between fluoromethylene units of the solutes and the solvent. From TFA to PFP, the effect decreased somewhat with the difluoromethylene unit introduction. In PEO, the effect of ester-group substituents was fairly selective. Acetate is the only one with a negative interaction parameter. The fluoromethylene unit in TFA and PFP introduced unfavorable interactions with PEO causing χ to increase. An additional fluoromethylene unit now leads to considerably unfavorable interaction as can be seen by the differences between TFA and PFP. The differences in the effect of fluoromethylene units is most distinguishable in the polar PEO phase. Finally, the difference between *tert*-butoxyl and TMSE was small. This should not be surprising because their structural interactions were quite similar.

5.4. Excess Properties of *n*-Alkanes and Aromatics.

Reduced excess enthalpy and residual entropy were calculated with eqs 7 and 8 and are listed in Table 5. In many discussions of solution thermodynamics or chemical kinetics, results frequently are presented using plots of enthalpy vs entropy.^{73,74} However, Krug et al.⁷⁵ demonstrated that, when enthalpies are calculated through the temperature dependence of the free energies, propagated errors usually result to give a straight line with a slope equal to the average temperature of the experimental measurements. Therefore, statistical errors tend to bias the extrathermodynamic relationship unless the slope of the enthalpy–entropy plot happens to be different from the average of the experimental temperatures. Krug et al. suggested a simple way to minimize the influence of such experimental errors. On the basis of statistical considerations, they concluded that enthalpy–free energy plots are more critical criteria for evaluating relationships between entropy and enthalpy than the earlier frequently used conventional enthalpy–entropy plots.⁷⁵ Plots using free energies have an added advantage in that free energies

TABLE 5: Reduced Residual Enthalpy of Solution (χ_H) and the Reduced Residual Entropy of Solution (χ_S) at 90 °C for Solutes in Polymers

solutes	DC-200		DC-550		QF-1		PEO	
	χ_H	χ_S	χ_H	χ_S	χ_H	χ_S	χ_H	χ_S
<i>n</i> -heptane	0.097	0.230	0.231	0.309	0.846	0.628	2.733	-0.780
<i>n</i> -octane	0.205	0.176	0.403	0.159	1.154	0.460	3.114	-1.016
<i>n</i> -nonane	0.290	0.141	0.519	0.072	1.730	0.043	3.502	-1.258
benzene	0.335	0.228	-0.132	0.453	0.401	0.473	-0.225	0.478
toluene	0.372	0.209	-0.063	0.376	0.364	0.628	0.134	0.274
<i>o</i> -xylene	0.523	0.155	0.039	0.306	0.717	0.411	0.452	0.065
1-methyl-3-ethylbenzene	0.507	0.152	0.029	0.316	0.996	0.329	0.864	-0.123
<i>n</i> -butyl acetate	0.394	0.165	-0.586	0.823	-0.123	0.593	0.451	0.049
cyclohexyl acetate	0.389	0.176	-0.381	0.533	0.324	0.342	0.660	-0.016
<i>m</i> -tolyl acetate	1.879	-0.419			0.194	0.750		
<i>p</i> -tolyl acetate	1.786	-0.333			0.340	0.576		
<i>n</i> -butyl TMSE	-0.204	0.439	-0.054	0.451	0.872	0.444	2.286	-0.499
cyclohexyl TMSE	0.625	-0.330	0.238	0.064	1.563	-0.092	2.550	-0.775
<i>m</i> -tolyl TMSE	-0.187	0.746			0.295	0.942	0.744	0.200
<i>p</i> -tolyl TMSE	-0.193	0.735			0.364	0.892	0.729	0.179
<i>n</i> -butyl TFA	1.162	-0.406	0.555	0.081	-0.037	0.455	1.303	0.044
cyclohexyl TFA	2.081	-1.476	-0.078	0.467	0.167	0.224	1.438	0.229
<i>m</i> -tolyl TFA	1.257	-0.314	0.573	0.135	0.078	0.566	0.033	0.704
<i>p</i> -tolyl TFA	1.286	-0.316	0.599	0.135	0.259	0.422	0.018	0.723
<i>n</i> -butyl PFP	0.729	0.024	0.370	0.508	-0.047	0.525	1.710	0.046
cyclohexyl PFP	1.236	-0.602	0.704	-0.114	0.661	-0.104	2.620	-0.891
<i>m</i> -tolyl PFP	0.990	-0.127	0.557	0.224	-0.237	0.859	0.674	0.544
<i>p</i> -tolyl PFP	1.101	-0.264	0.613	0.137	-0.075	0.678	0.798	0.388
<i>n</i> -butyl <i>tert</i> -butyl ether	0.024	0.283	-0.318	0.678	1.107	0.199	2.049	-0.463

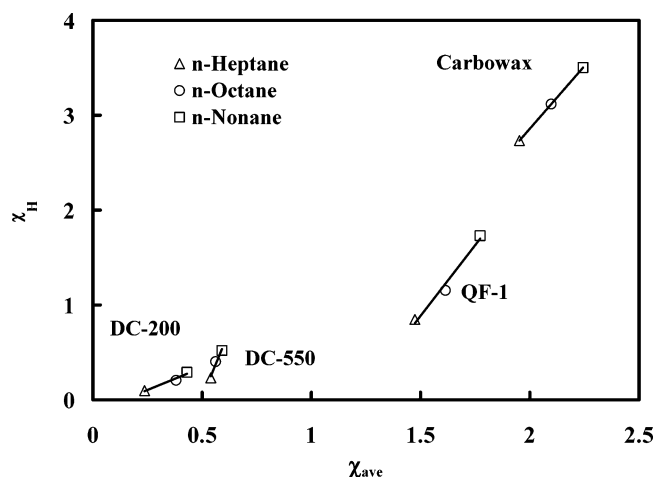


Figure 3. Plots of χ_H vs χ_{ave} at 90 °C for *n*-alkanes in four liquid phases. (Δ) *n*-Heptane; (\circ) *n*-octane; (\square) *n*-nonane. Lines are drawn to indicate linearity and varying slopes.

in solution thermodynamic studies are linearly related to the logarithms of activation coefficients. It is these net activity coefficients that are most pertinent to separation processes. Li and Carr⁷³ in a more recent discussion of enthalpy–entropy compensation in gas chromatography noted that for the enthalpy-free energy plots only solutes belonging to a homologous series produce linear free energy relationships.

In Figure 3, reduced excess enthalpies, χ_H , vs reduced free energies, χ_{ave} , of the *n*-alkanes in four polymer solvents are plotted. χ_{ave} is the average value of χ at 80 and 100 °C. *n*-Alkanes give straight lines for all solvents, thus meeting the more rigid criteria. These results are not surprising since *n*-alkanes are the simplest homologous series among organic compounds. Indeed, the regular behavior of *n*-alkanes is the basis of the well-known Kovats reference system in gas chromatography for reporting retention volumes. The linearity of the enthalpy and entropy of solution plots for homologous series such as *n*-alkanes, cyclic alkanes, or β -ketones series by carbon number have been demonstrated for several liquid phases.^{76,77} However, both enthalpy of solution and entropy of solution involve a large phase change quantity and a small excess quantity. Plots of the excess properties would seem to be more appropriate for discussing solution behaviors.

Reduced excess enthalpy, χ_H , and reduced residual entropy, χ_S , of *n*-alkanes in DC-200 and DC-550 are both low because interactions are probably dominated by methyl–methyl (methylene) interactions. That DC-550 has a higher χ_H than DC-200 can be explained by unfavorable aromatic–methyl hydrocarbon contacts in the solution process, which are absent in the DC-200 system. DC-550 is also characterized by a higher rate of decrease of χ_S for each additional methylene unit, which can arise from the destruction of a phenyl–phenyl interactions and a randomness increase in DC-550 during the solution process for large molecules. The change of enthalpy and entropy of solutions of *n*-alkanes in the two silicone polymers correlate differently and result in two lines with different slopes as shown in Figure 3.

n-Alkanes give very high χ values in PEO and QF-1. Their enthalpy-free energy lines are near parallel, but PEO gives a higher χ_H than QF-1. The positive values of χ_H are a result of differences in strength of dipole interactions between solutes, solvents, and solute–solvent pairs. The values of χ_H do increase linearly as carbon numbers increase. Values of χ_S are of a different sign; they are positive in QF-1 and negative in PEO, but in both polymers, χ_S decreased as carbon numbers increase.

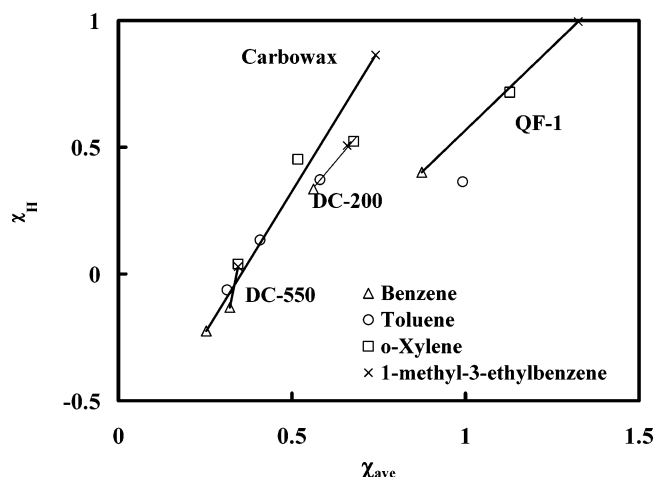


Figure 4. Plots of χ_H vs χ_{ave} at 90 °C for aromatics in four liquid phases. (Δ) Benzene; (\circ) toluene; (\square) *o*-xylene; (\times) 1-methyl-3-ethylbenzene. Lines are drawn to show values varying from linear relationship.

The value of χ_S also vary almost linearly with carbon number similar to values of χ_H . The decreasing trend of χ_S as carbon numbers increase probably also include contributions from the destruction of ordered solvent structures due to increasing size of the solute molecules. It can be noted that QF-1 contains fluorocarbon substituents and methyl groups on a siloxane chain. Its structure probably involves some segregation with local hydrocarbon and fluorocarbon domains.⁸ The fact that χ_S values for *n*-alkanes in QF-1 decreased with increasing carbon number probably resulted from a destruction of order during the dissolution process of *n*-alkanes within small, ordered hydrocarbon domains of QF-1 by excluded-volume interaction. This is similar to previously noted χ_S values in DC-550 except that in QF-1 the rate of decrease of χ_S is larger.

The enthalpy-free energy relations for aromatic solutes are plotted in Figure 4. The data points are well scattered because they do not belong to a homologous series. With a polarizable aromatic ring, both χ_H and χ_{ave} values are higher than those for *n*-alkanes in DC-200 and smaller than those in DC-550. DC-200 gives low contact energy differences for *n*-alkanes because of similarities in the hydrocarbon–hydrocarbon contacts. In contrast, DC-550 gives lower χ_H and χ_{ave} values for aromatic solutes because of possibilities for aromatic–aromatic interactions. In DC-200, *o*-xylene had the highest χ value among all aromatics at both 80 and 100 °C which perhaps represents a “squeezing effect”. This might be attributed to the higher dipole moment of *o*-xylene.²⁴ However, this effect is not great and appears to be absent in other solvents.

Aromatic solutes in PEO and QF-1 are characterized by a wide variation in χ and χ_H values. Benzene, a compact polarizable compound, has the lowest χ value among aromatics in all polymers. With increasing side chains, the interaction parameter seems to increase substantially. QF-1 always gives higher χ values as a result of unfavorable aromatic–hydrocarbon and aromatic–fluorocarbon contacts. In contrast, PEO is known to interact with polarizable aromatic rings. QF-1 also gives higher χ_S values than PEO as can also be seen from Table 5. Aromatic dissolution in the QF-1 structure tends to be unfavorable because of the absence of favorable interaction with hydrocarbon or fluorocarbon. The steep linearly increasing values for χ_H and χ_{ave} for *n*-alkanes and aromatics in PEO and QF-1, with increasing substituents and molecular size, suggest that these interactions may be related to the excluded-volume

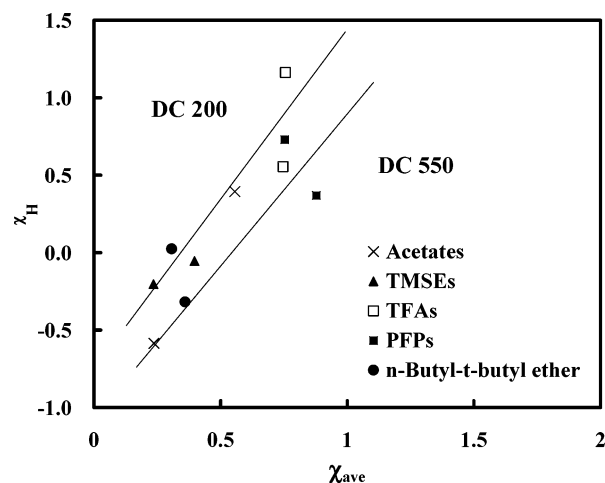


Figure 5. Plots of χ_H vs χ_{ave} at 90 °C for *n*-butyl derivatives in DC-200 (upper line) and DC-550 (lower line). (x) Acetates; (\blacktriangle) trimethylsilyl ethers; (\square) trifluoroacetates; (\blacksquare) pentafluoropropionates; (\bullet) *n*-butyl *tert*-butyl ether. Lines are drawn to show trends and scatter for some compounds.

interaction, which is increased when the size of the solute molecules increases.

5.5. Excess Properties of Derivatives. The derivatives here include four parent compound types: *n*-butyl, cyclohexyl, *m*-tolyl, and *p*-tolyl groups, with four types of derivatizing agents giving acetates, TMSEs, TFAs, and PFPs. As indicated earlier, *n*-butyl *tert*-butyl ether was included because of its structural similarity to *n*-butyl TSME. Because the derivatives are of “dual character”, simple linear relations between excess properties can be distorted by the complexities arising from varying solution interactions and orientations.

The *n*-butyl derivative group is the only one that seems to exhibit a linear relationship in enthalpy-free energy plots. Figure 5 shows a comparison for the solvent pair DC-200 and DC-550. Two lines are drawn in Figure 5 to show the trend. In DC-550, relative to DC-200, the χ_S values are more positive since the line is lower. This is also true for almost all derivatives, as can be seen in Table 5, and can also be explained from the structures of the two solvents. The DC-550 used here contains one phenyl and three methyl groups for every two silicon atoms in the siloxane chain.⁴⁷ In the pure solvent, the phenyl group with methyl groups probably contact similar partners to minimize energy, producing a more ordered liquid structure. When a dual-character solute molecule is dissolved in the solvent matrix, it is probably incorporated within the solvent structure and localized to have different parts of the molecule contacting either methyl or phenyl groups to minimize energy. This process decreases entropy and is manifested with more positive χ_S values. This is opposite to the *n*-alkane dissolution in polymers mentioned earlier where destruction of order in solvent led to a lower χ_S .

The sequences for *n*-butanol derivatives are maintained for the two solvents except for the reversal of the acetate and TMSE. This is a result of the structure and properties of these solvents. DC-550 contains a polarizable phenyl group and favors acetate solution. DC-200, with only methyl substituents on silicon atoms, favors the more similar TMSE. In comparison to acetate, the χ_H value of the TFA derivatives significantly increased for both solvents; however, the resulting overall χ values which include entropy effects are close in both polymers. This then is a true enthalpy–entropy compensation effect. *n*-Butyl PFP give lower χ_H values than *n*-butyl TFA in both DC-200 and DC-550. The additional fluoromethylene unit has little effect on

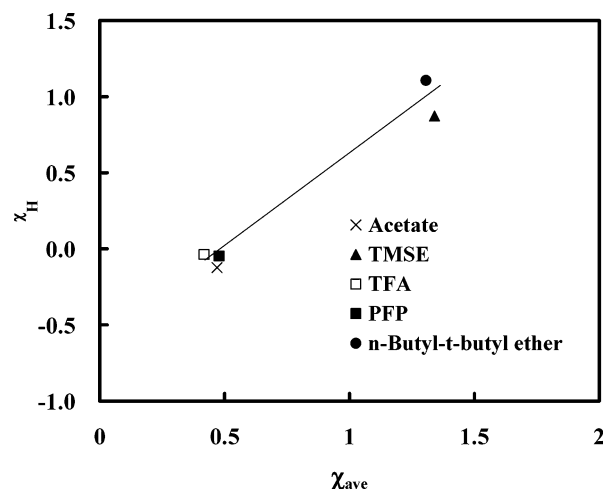


Figure 6. Plots of χ_H vs χ_{ave} at 90 °C for *n*-butyl derivatives in QF-1. (x) Acetate; (\blacktriangle) trimethylsilyl ether; (\square) trifluoroacetate; (\blacksquare) pentafluoropropionate; (\bullet) *n*-butyl *tert*-butyl ether. Line is drawn to indicate linearity and some scatter.

reducing the interaction of the ester group, but the more heavily fluorinated PFP's increase the repulsion energy in the pure liquid states; this is reflected as less positive excess enthalpy for solution as well as lower solubility parameters for solutes.¹²

The enthalpy-free energy relation of *n*-butanol derivatives for QF-1 was shown in Figure 6. The slope is about 1.3, lower than the slopes of lines in Figure 5. In QF-1, fluoroesters and acetate have very small χ_H values with positive χ_S values. These positive χ_S values may again result from localization of solutes into the more ordered structure of QF-1. Ester interactions seem to be more energetically favorable with QF-1 than ethers and lead to a lower χ_H values. *n*-Butyl *tert*-butyl ether and *n*-butyl TMSE have very high χ_H and low χ_S values in both solvents because without dual character they do not favor orientation in the QF-1 structure. The multicomponent character of QF-1 is evident from examining dissolution of these different types of solutes. Data for PEO do not follow a simple relation and are not compared here in Figure 6.

With only a few exceptions, cyclohexyl derivatives usually have higher χ_H and lower χ_S values than the corresponding *n*-butyl derivatives reflecting effects of difference in hydrocarbon structure. The largest difference between cyclohexyl and butyl derivatives occurs with the TFA derivatives when they are dissolved in DC-200; the difference in the χ_H values is about 0.9, which is striking. The effect of a carbon number difference may result in a decrease of χ values by about 0.2, but the remainder is still significant. The differences for χ_S values also imply that there is a large corresponding difference in residual entropies. This effect apparently originates from the shape of the parent hydrocarbons rather than from carbon number. The effect of molecular shape on solution thermodynamics has been demonstrated by Patterson et al.^{13,14} in their study of hydrocarbon solute and solvent representatives of different types of branched isomers. They found that a branched molecule usually shows a positive excess enthalpy, proportional to the degree of branching, when dissolved in *n*-alkane. Positive entropies of solution (negative χ_S) usually result from the destruction of local solvent order. The cyclohexyl group has a geometry different from that of solvents here and thus is expected to bring an enthalpy decrease and an entropy increase because of structural reorganization during solution. In addition, the relatively flat overall structure of cyclohexyl derivatives may result in a solute liquid of well-organized, overlapped form, which when dissolved in another liquid would result in a large entropy increase. The

TABLE 6: Separation Factors of Derivatives and Their Components: Vapor Pressure Ratios of Solutes, Interaction Parameters of Meta Derivatives, and Differences between Meta and Para Derivatives at 100 °C for Four Polymers

derivatives		DC-200	DC-550	QF-1	PEO
acetate	χ_{m-}	1.410	0.750	0.936	0.068
$P_{m-}/P_{p-} = 1.023$	$\chi_{m-} - \chi_p$	0.006	0.011	0.031	0.025
	separation factor α^a	1.026	1.031	1.052	1.046
TSME	χ_{m-}	0.564	0.308	1.225	0.921
$P_{m-}/P_{p-} = 1.047$	$\chi_{m-} - \chi_p$	0.017	0.030	-0.018	0.035
	separation factor α^a	1.065	1.079	1.030	1.084
TFA	χ_{m-}	0.907	0.688	0.639	0.732
$P_{m-}/P_{p-} = 1.081$	$\chi_{m-} - \chi_p$	-0.029	-0.026	-0.030	-0.004
	separation factor α	1.050	1.052	1.047	1.075
PFP	χ_{m-}	0.883	0.762	0.625	1.196
$P_{m-}/P_{p-} = 1.029$	$\chi_{m-} - \chi_p$	0.029	0.033	0.023	0.040
	separation factor α^a	1.060	1.061	1.051	1.069

^a α is the retention volume of para derivative/retention volume of meta derivative.

condensed dual character of cyclohexyl derivatives, (e.g., the TFAs) also favors the formation of relatively organized pure solute liquids.

5.6. Separation of Aromatic Isomers. χ values for aromatic derivatives follow no simple correlation because both the aromatic ring and the derivatizing group are involved in the interaction with solvent as well as with each other. The main effect of the aromatic ring was shown in Table 4. Small, nonlinear ring-derivatizing group interactions may still be included in the remainder, which may be important in determining the separation factor for aromatic isomers. The values of χ for the meta isomer for each derivative and each solvent are given in Table 6. The differences between isomers are also computed and listed. Also listed in the Table are the vapor pressure ratios of solutes and the separation factor calculated as the ratio of retention volume, $\alpha = V_{g,p}/V_{g,m} = P_{m-}/P_{p-} \exp(\chi_{m-} - \chi_p)$. It can be seen that each derivatizing group gives a varying contribution, which is also influenced by solvent. Acetates give a contribution to χ values, which vary from 1.410 to 0.068, when the stationary phase is changed from nonpolar silicones to strongly polar PEO. Other derivatives give moderate values for χ . In general, the selection of the derivatizing group for a separation effect should be made with consideration of the stationary phase.²¹ Generally, a positive interaction parameter providing higher elution speed is preferred.

The differences between χ values of isomers are important because of their separation implications. PFP and TMSE gave a high difference with a positive sign. Since the vapor pressures of meta isomers are generally higher than para isomers, only positive differences in the interaction parameter tend to be useful. TFA derivatives had the highest vapor pressure ratio, but the elution difference between meta and para derivatives is less favorable. This situation was observed for other stationary phases.¹² When combined with vapor pressure, the separation ratio is highest for TMSE derivatives in PEO. The results listed in Table 6 are, however, consistent with the guidelines for choosing stationary phases proposed earlier.²¹ Usually, a stationary phase with a solubility parameter differing from the isomers will tend to give higher separation factors. TMSE, TFA, and PFP give a high meta-para difference on PEO, according to this approach. However, acetates do not obey this generalization in DC-200 and DC-550. Acetates have high solubility parameters, but their aromatic derivatives did not give good resolution with low solubility parameter silicone phases. The properties of tolyl acetates are quite different from tolyl PFPs. With fluorine substituents, tolyl PFP has dual character, e.g., two different groups and low contact energies between them. Tolyl acetates contain two groups with different properties which can still interact with each other. The resulting solute interactions

seem unfavorable for isomer separation. Also, the attractive solute interactions lower vapor pressures and are not favorable for elution and chromatographic practice. Therefore, in the selection of overall systems, one might choose derivatives giving low cohesive energy to match a stationary phase with high cohesive energy to achieve separation in the most expedient fashion for gas chromatography and similar applications. With liquid chromatography, these and more complex solution effects might be reinforced.

6. Conclusions

Retention volumes, V_g^T , are measured, and Flory-Huggins parameters, χ , the reduced residual enthalpy of solution, χ_H , and reduced residual entropy of solution, χ_S , of a variety of solutes in silicone-type polymeric solvents and PEO are calculated at 80 and 100 °C. For derivatives, the Flory-Huggins interaction parameter can be summed based on the structural units. A linear enthalpy-free energy relation is found for *n*-alkanes, aromatic hydrocarbons, and *n*-butyl derivatives. The derivatives, many of which are molecules of two groups of disparate properties (dual character), show some trend in solution thermodynamic properties. These deviations can be related somewhat to the structures of solvents, solutes, and the nature of the solution processes. With the variety of systems studied here, the effectiveness of gas chromatography for studying polymer solution properties and thermodynamic properties of molecules of complex structures is demonstrated again. From screening derivatives with different intermolecular energies, we find formation of derivatives with highly favorable intermolecular energy, such as tolyl acetates, do not tend to give good separation factors with some silicone-based liquid phases. However, favorable separation factors tend to be favored by low intermolecular energy derivatives matched with liquid phases of high intermolecular energy. This observation agrees with guidelines for choosing liquid phases based on simple theory that were explained and proposed earlier.²¹

References and Notes

- (1) Conder, J. R.; Young, C. L. *Physicochemical Measurements by Gas Chromatography*; Wiley: New York, 1979.
- (2) Laub, R. J.; Pecsok, P. L. *Physicochemical Applications of Gas Chromatography*; Wiley: New York, 1979.
- (3) Vilcu, R.; Leca, M. *Polymer Thermodynamics by Gas Chromatography*; Vasilescu, V., translator; Amsterdam: Elsevier: 1990.
- (4) Al-Saigh, A. Z. *Polym. News* **1994**, 19, 269-279.
- (5) Gray, D. G.; Guillet, J. E. *Macromolecules* **1973**, 6, 223-227.
- (6) Romansky, M.; Guillet, J. E. *Polymer* **1994**, 35, 586-589.
- (7) Guillet, J. E. In *New Development in Gas Chromatography*; Purnell, J. H., Ed.; Wiley: New York, 1979; p 187.
- (8) Langer, S. H.; Patton, J. E. *J. Phys. Chem.* **1972**, 76, 2159-2169.

- (9) Thede, R.; Below, E.; Haberland, D.; Langer, S. H. *Chromatographia* **1997**, *45*, 149–154.
- (10) Langer, S. H.; Sheehan, R. J. *J. Chem. Eng. Data* **1969**, *14*, 248–250.
- (11) Knapp, D. R. *Handbook of Analytical Derivatizing Reactions*; Wiley: New York 1979.
- (12) Langer, S. H.; Sheehan, R. J.; Huang, J. C. *J. Phys. Chem.* **1982**, *86*, 4605–4618.
- (13) Barbe, M.; Patterson, D. *J. Phys. Chem.* **1978**, *82*, 40–46.
- (14) P. de St. Romain, P.; Van, H. T.; Patterson, D. *J. Chem. Soc., Faraday Trans., I* **1979**, *75*, 1700–1714.
- (15) Patterson, D. *Thermochim. Acta* **1995**, *267*, 15–27.
- (16) Aicart, E.; Van, H. T.; Andreoli-Ball, L.; Patterson, D. *J. Solution Chem.* **1994**, *23*, 1183–1203.
- (17) Trejo, L. M.; Costas, M.; Patterson, D. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3001–3008.
- (18) Andreoli-Ball, L.; Sun, S. J.; Trejo, L. M.; Costas, M.; Patterson, D. *Pure Appl. Chem.* **1990**, *62*(11), 2097–2106.
- (19) Vrbka, P.; Dohnal, V.; Trejo, L. M.; Costas, M. *Fluid Phase Equilib.* **1997**, *137*, 133–140.
- (20) Langer, S. H. *Anal. Chem.* **1967**, *39*, 524–525.
- (21) Langer, S. H.; Sheehan, R. J. In *Progress in Gas Chromatography*; Purnell, J. H., Ed.; Interscience: New York, 1968; pp 289–323.
- (22) Langer, S. H.; Purnell, J. H. *J. Phys. Chem.* **1963**, *67*, 263–270.
- (23) Langer, S. H.; Purnell, J. H. *J. Phys. Chem.* **1966**, *70*, 904–909.
- (24) Conder, J. R.; Langer, S. H. *Anal. Chem.* **1967**, *39*, 1461–1464.
- (25) McGlashan, M. L.; Potter, D. J. B. *Proc. R. Soc. London Ser. A* **1962**, *267*, 478–500.
- (26) McGlashan, M. L.; Wormald, C. J. *Trans. Faraday Soc.* **1964**, *60*, 646–652.
- (27) Guggenheim, E. A.; Wormald, C. J. *J. Chem. Phys.* **1965**, *42*, 3773–3780.
- (28) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: New York, 1953.
- (29) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7–29.
- (30) Guggenheim, E. D. *Trans. Faraday Soc.* **1945**, *44*, 1007–1012.
- (31) Rossini, F. P.; Mair, B. J.; Streiff, A. J. *Hydrocarbons from Petroleum*; Reinhold Publishing: New York, 1953.
- (32) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
- (33) Sheehan, R. J. Ph.D. Thesis, Department of Chemical Engineering, University of Wisconsin, 1968.
- (34) Galin, M. *Macromolecules* **1977**, *10*, 1239–1244.
- (35) Summers, S. W.; Tewari, Y. B.; Schreiber, H. P. *Macromolecules* **1972**, *5*, 12–16.
- (36) Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* **1974**, *7*, 530–535.
- (37) Lichtenthaler, R. N.; Prausnitz, J. M.; Su, C. S.; Schreiber, H. P.; Patterson, D. *Macromolecules* **1974**, *7*, 136.
- (38) Lichtenthaler, R. N.; Liu, D. D.; Prausnitz, J. M. *Macromolecules* **1974**, *7*, 565–570.
- (39) Hammers, W. E.; de Ligny, C. L. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2065–2074.
- (40) Hammers, W. E.; Bos, B. C.; Vaas, L. H.; Loomans, Y. J. W. A.; de Ligny, C. L. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 401–417.
- (41) Ashworth, A. J.; Chien, C. F.; Furio, D. L.; Hooker, D. M.; Kopenčič, M. M.; Laub, R. J.; Price, G. J. *Macromolecules* **1984**, *17*, 1090–1084.
- (42) Roth, M.; Novák, J. *Macromolecules* **1986**, *19*, 364–369.
- (43) Price, G. J.; Guillet, J. E. *J. Solution Chem.* **1987**, *16*, 605–613.
- (44) Roth, M. *J. Polym. Sci. Polym. Ed.* **1990**, *28*, 2715–2719.
- (45) Roth, M.; Novák, J.; David, P.; Novotny, M. *Anal. Chem.* **1987**, *59*, 1490–1494.
- (46) Parcher, J. F.; Hansbrough, J. R.; Koury, A. M. *J. Chromatogr. Sci.* **1978**, *16*, 183–189.
- (47) Humpa, O.; Uhdeová, J.; Roth, M. *Macromolecules* **1991**, *24*, 2514–2517.
- (48) Petri, H. M.; Schuld, N.; Wolf, B. A. *Macromolecules* **1995**, *28*, 4975–4980.
- (49) Schuld, N.; Wolf, B. A. *J. Polym. Sci., Part B: Polym. Physics* **2001**, *39*, 651–662.
- (50) Tan, Z.; Jaeger, R.; Vancso, G. J. *Polymer* **1994**, *35*, 3230–3236.
- (51) Tan, Z.; Vancso, G. J. *Macromolecules* **1997**, *30*, 4665–4673.
- (52) Coca, J.; Rodríguez, J. L.; Medina, I.; Langer, S. H. *J. Chem. Eng. Data* **1989**, *34*, 280–284.
- (53) Galin, M. *Polymer* **1983**, *24*, 865–870.
- (54) Saeki, S.; Bonner, D. C. *Polymer* **1978**, *19*, 319–324.
- (55) Fernández-Berridi, M. J.; Otero, T. F.; Guzmán, G. M.; Elorza, J. M. *Polymer* **1982**, *23*, 1361–1366.
- (56) Fernández-Berridi, M. J.; Guzmán, G. M.; Iruin, J. J.; Elorza, J. M. *Polymer* **1984**, *24*, 417–422.
- (57) Etcheberria, A.; Elorza, J. M.; Iruin, J. J.; Macro, C.; Gomez, M. A.; Fatou, J. G. *Eur. Polym. J.* **1993**, *29*, 1483–1487.
- (58) Elorza, J. M.; Fernandez-Berridi, M. J.; Iruin, J. J.; Guzmán, G. M. *Polym. Eng. Sci.* **1984**, *24*, 287–290.
- (59) Klein, J.; Jeberien, H. E. *Makromol. Chem.* **1980**, *181*, 1237–1249.
- (60) Chang, Y. H.; Bonner, D. C. *J. Appl. Polym. Sci.* **1975**, *19*, 2439–2455, 2457–2472.
- (61) Cheng, Y. L.; Bonner, D. C. *Macromolecules* **1974**, *7*, 687–690.
- (62) Galin, M. *Polymer* **1995**, *36*, 3533–3539.
- (63) Roth, M. *Macromolecules* **1990**, *23*, 1696–1700.
- (64) Becerra, M. R.; Fernández-Sánchez, E.; Fernández-Torres, A.; Garca-Dominguez, J. A.; Santiuste, J. M. *Macromolecules* **1992**, *25*, 4665–4670.
- (65) Demathieu, C.; Chehimi, M. M.; Lipskier, J.-F. *Sens. Actuators, B* **2000**, *62*, 1–7.
- (66) Patterson, D.; Tewari, Y. B.; Schreiber, H. P.; Guillet, J. E. *Macromolecules* **1971**, *4*, 356–359.
- (67) Flory, P. J.; Orwoll, R. A.; Vrij, A. J. *Am. Chem. Soc.* **1964**, *86*, 3507–3520.
- (68) Allen, G.; Gee, G.; Wilson, G. J. *Polymer* **1960**, *1*, 456–466.
- (69) Biroš, J.; Zeman, L.; Patterson, D. *Macromolecules* **1971**, *4*, 30–35.
- (70) Freeman, P. I.; Rowlinson, J. S. *Polymer* **1960**, *1*, 20–26.
- (71) Pierotti, G. J.; Deal, C. H.; Derr, E. L. *J. Am. Chem. Soc.* **1956**, *78*, 2989–2998.
- (72) Pierotti, G. J.; Deal, C. H.; Derr, E. L.; Porter, P. E. *Ind. Eng. Chem.* **1959**, *51*, 95–102.
- (73) Li, J.; Carr, P. W. *J. Chromatogr. A* **1994**, *670*(1–2), 105–116.
- (74) Bell, R. P. *Trans. Faraday Soc.* **1937**, *33*, 496–501.
- (75) Krug, R. R.; Hunter, R. H.; Grieger, R. A. *J. Phys. Chem.* **1976**, *80*, 2335–2451.
- (76) Meyer, E. F.; Weiss, R. H.; Gens, T. H. *J. Chem. Thermodyn.* **1977**, *9*, 439–444.
- (77) Meyer, E. F.; Weiss, R. H. *J. Chem. Thermodyn.* **1977**, *9*, 431–438.