Henry's Law Coefficients for Monomers and Selected Solvents in Amorphous Tetrafluoroethylene−Hexafluoropropylene Copolymers

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This paper presents Henry's law coefficients for tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) monomers, their dimers, and a number of potential process solvents in amorphous TFE−HFP copolymers. A standard inverse gas chromatographic method was used for the measurements. Results are presented to validate the experimental techniques and data reduction methods by comparison with published literature values for polystyrene with selected solvents. The specific amorphous TFE−HFP copolymer used for these measurements was characterized by fluorine NMR as consisting of 53 mol % HFP and 47 mol % TFE with 15% of the HFP as diads. A number-average molecular weight of 104 000 with a polydispersity of 2.81 was determined by gel permeation chromatography analysis. A total of 19 binary systems were measured for this polymer at 4−6 temperatures over the range of (321 to 511) K. The experimental data are correlated by fitting with an Arrhenius temperature dependency.

Introduction

Amorphous perfluorinated polymers are useful materials in various applications because of their unusual surface properties and the relative ease of coating or encapsulating plastic or metal substrates with such polymers. In particular, amorphous copolymers of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP)[1,2] are desirable for applications such as coatings in certain electronic devices and as polymer processing aids. These copolymers have high solubility in suitable liquid solvents, are optically clear, and can be used to produce exceptionally thin coatings and films with properties such as a low refractive index and dielectric constant. Solubility estimates for residual monomers and potential solvents in these polymers are important for the development of manufacturing processes for these materials as well as for product evaluations in various applications.

In support of such efforts, pertinent Henry's law coefficients have been measured using a standard inverse gas chromatographic technique. A total of 19 binary systems are presented for a representative amorphous TFE−HFP copolymer at 4−6 temperatures over the range of (321 to 511) K. These binaries include the polymer plus the monomers, their dimers, and a number of potential process solvents. The experimental data are correlated by fitting with an Arrhenius temperature dependency.

Theoretical Basis

Inverse gas chromatography is a standard technique to measure infinite dilution interactions for solutes in concentrated polymer solutions. Young[3] presented an early review paper describing the use of gas chromatography (GC) for measuring a variety of thermodynamic properties including activity coefficients. Smidsrød and Guillet[4] presented an early study describing the interactions of acetic acid, butyl alcohol, chloronaphthalene, naphthalene, and hexadecane with poly(*N*-isopropylacrylamide). Patterson et al.[5] applied gas chromatography to obtain thermodynamic properties of polymer solutions and presented various equations for calculating thermodynamic quantities from experimental measurements. Lenoir et al.[6] reported Henry's law coefficients for 12 gases in both polar and nonpolar solvents. Newman and Prausnitz[7,8] discussed the measurement of polymer−solute interactions in several systems including polystyrene, polyethylene, polyisobutylene, and copolymers of ethylene with vinyl acetate and propylene. Schreiber[9] presented a study of interactions of various aliphatic and aromatic solvents with polyethylene using gas chromatography. Liu and Prausnitz[10,11] measured Henry's law coefficients for a variety of solutes in polyethylene, ethylene−vinyl acetate copolymers, and poly(vinyl acetate). A more recent paper by Hadj Romdhane and Danner[12] presented experimental results for a wide variety of polar and nonpolar organic solutes in both polybutadiene and polyisoprene. Hadj Romdhane et al.[13] extended the technique for calculating fundamental thermodynamic interaction data for various solvents with two styrene−butadiene−styrene triblock copolymers including Flory−Huggins interaction parameters, partial molar enthalpies of mixing, and enthalpies of solution. Hadj Romdhane and Danner[14] provided a further extension of the method to determine diffusion coefficients of low molecular weight penetrants in polymers.

Newman and Prausnitz[8] give a concise presentation of the theoretical equations needed to reduce the experimental data to calculate Henry's law coefficients. At low solute concentrations, the Henry's law coefficient can be calculated directly from gas chromatographic data by the equation

$$H = \left(\frac{P_1^{\,s}}{W_1}\right) = \frac{RT}{V_g M_1} \tag{1}$$

where H is the mass fraction Henry's law coefficient, P_1^{s} is the solute vapor pressure over the polymer/solute mixture, W_1 is the mass fraction of solute, R is the universal gas constant, T is the column temperature, and M_1 is the solute molecular weight.

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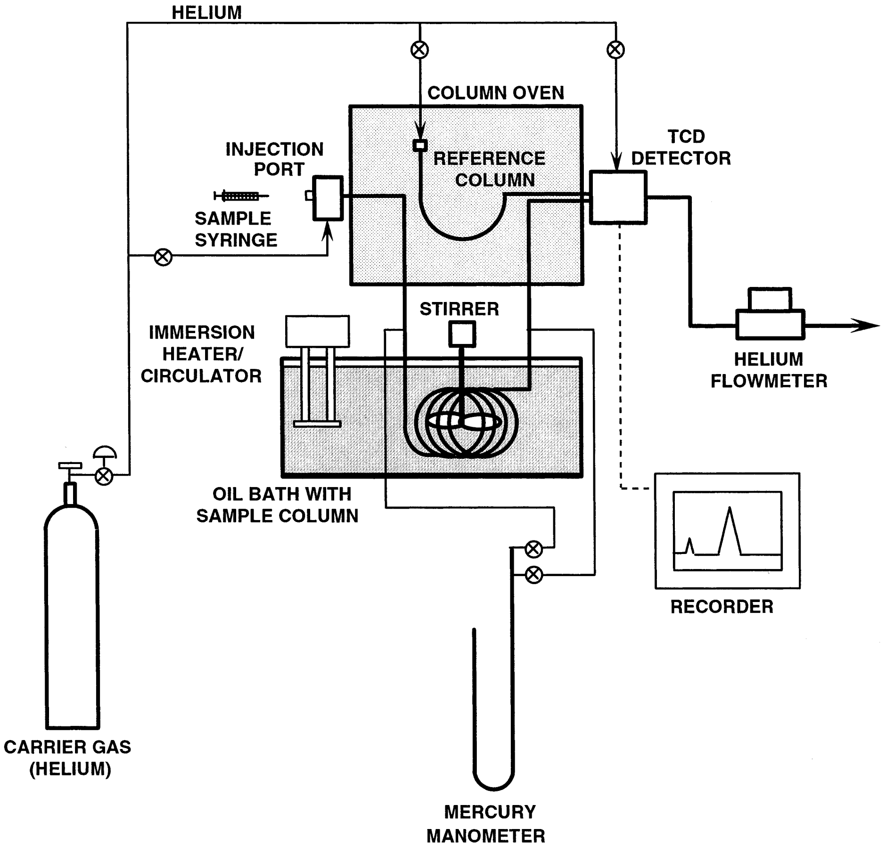

Figure 1. Schematic diagram of the gas chromatographic apparatus.

The specific retention volume V_g is given by

$$V_g = Q(t_s - t_r)\frac{f_p}{W_2} \tag{2}$$

where V_g is the solute specific retention volume, Q is the carrier gas volumetric flow rate at the column temperature and column outlet pressure, t_s is the retention time of the solute sample in the GC column, t_r is the retention time of an inert, nonadsorbing reference sample in the GC column, and W_2 is the polymer mass in the column.

The parameter f_p, known as the James−Martin compressibility factor, corrects for the pressure drop across the GC column and is given by Purnell:[15]

$$f_p = \frac{3}{2}\frac{[(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]} \tag{3}$$

where P_i is the absolute column inlet pressure and P_o is the absolute column outlet pressure.

The effluent volumetric flow rate from the GC column must be corrected to the column temperature and outlet pressure to give the desired column volumetric flow rate, Q. Correcting for these effects gives the following equation for calculating the column flow rate Q:

$$Q = Q_m\frac{P_{amb}}{P_o}\frac{T}{T_{amb}} \tag{4}$$

where Q_m is the measured volumetric carrier gas flow rate, P_{amb} is the absolute ambient pressure, and T_{amb} is the ambient temperature.

Hadj Romdhane and Danner[12] present the following correlation for the infinite dilution mass fraction activity coefficient based on the thermodynamic requirement of equal fugacities of the solute in the vapor and polymer phases:

$$\gamma_w^\infty = \frac{RT}{V_g P_1^s M_1}\exp\left[-\frac{P_1^s(B_{11} - V_1)}{RT}\right] \tag{5}$$

where γ_w^∞ is the infinite dilution mass fraction activity coefficient, B_{11} is the second virial coefficient of the pure solute, and V_1 is the saturated liquid molar volume of the solute.

Equation 1 gives the mass fraction Henry's law coefficient of the solute at low concentrations in the polymer. Note that only the column temperature, the solute molecular weight, and the specific retention volume are needed to calculate this coefficient from chromatographic data. These can be readily obtained from experimentally measurable quantities. The additional pure-component physical properties P_1^s, B_{11}, and V_1 for the solute are required to calculate the infinite dilution mass fraction activity coefficient by eq 5.

Experimental Section

Figure 1 shows a schematic diagram of the gas chromatographic apparatus used in this work. The gas chromatograph was a Hewlett-Packard (HP) model 5880A (level 4) instrument equipped with a thermal conductivity detector and the standard model 5880A integrator. The thermal conductivity detector used a single filament that monitored both the reference and sample carrier gas flows. A third carrier gas flow was used to operate a modulator valve to alternately switch the reference and sample gas flows to the filament. Helium was used as the carrier gas, and a Humonics MicroFlo 20 mass flow meter was used to measure the gas flow rates. The flow meter was calibrated for helium by the manufacturer with a NIST-certified volumetric primary standard to an accuracy of about ±0.2%. The carrier gas flow rate was set at a measured value of approximately 5 cm^3/min using the flow meter and precision low-flow regulator valves. This flow rate was previously determined to be low enough to provide measured results sufficiently close to equilibrium values, within experimental error.

The sample column temperature was controlled to ±0.2 K by immersing the column in an external oil bath equipped with a Haake model F3 immersion heater/circulator and temperature controller rated for (293 to 543) K. Dow Corning 550 fluid was used as the heat transfer fluid in the bath. A separate ECS model 800-261 high-temperature alarm was used as a secondary shutoff in the event of overheating. Additional agitation was provided in the oil bath by an impeller mounted inside the coiled column. This stirrer was driven by a T-Line 1/18-horsepower electric laboratory stirrer motor. The column temperature was measured to within ±0.1 K by a type K thermocouple suspended in the oil bath. This thermocouple and corresponding thermometer (Omega model DP460) were calibrated as a unit using either certified ASTM-grade precision mercury-in-glass thermometers or a 4-wire, 100 Ω secondary platinum resistance thermometer standard (Hart Scientific model 5682) calibrated by the manufacturer relative to a NIST-certified primary standard. Experiments were conducted at temperatures ranging from (321 to 511) K. The 3.2 mm o.d. 316 stainless steel (SS) tubing connecting the analytical column to the GC oven was heated with electrical heating tape controlled by a rheostat to a temperature approximating that of the analytical column. The reference column (3.2 mm o.d. × 0.5 m long SS tubing containing 2% OV-101) was heated in the GC oven to a temperature comparable to that of the oil bath. The injection port and the detector were heated to (498 to 573) K depending on the sample temperature. These components were generally maintained at least 50 K above the sample temperature.

The inlet and outlet column pressures were measured to within 100 Pa by a mercury manometer. The solute samples were injected into the GC injection port through a silicone rubber septum using either a 1-μL (for liquid solutes) or 25-μL Gastight (for gas samples) Hamilton syringe. Sample sizes of 0.1 μL for liquid solutes and 5 μL for gas solutes were used based on results of a previous study showing these to be acceptable for reproducibility but sufficiently small so as to not influence measured retention times. Nitrogen was used as a reference gas to determine the transfer time ("dead" time) in the column. Gas-phase samples were stored in 150-mL sample cylinders equipped with isolation valves, a relief valve, and a pressure gauge, and syringes were loaded directly from these cylinders prior to injection. Each sample cylinder was initially flushed and then filled to about 3 bar with the sample gas. One end was then sealed with a silicone rubber septum in a Swagelok compression fitting, allowing an approximately 2-mL gas sample to be trapped between the valve and septum. This cavity was evacuated through a syringe needle connected to a vacuum and then refilled via the sample valve several times before collecting a sample for injection.

The measurements were conducted with 3−5 replicates in order of ascending temperature, and the low temperature point was repeated to ensure repeatability following the measurements at the higher temperatures. These additional replicates were repeatable within the experimental error of the initial values.

Table 1. Description of Polymer Samples

characterization		polystyrene standard[a]	amorphous TFE−HFP copolymer
molecular weight[b]	M_n	86700	104000
	M_w	90100	292000
	M_v		260000
	M_w/M_n	1.04	2.81
composition[c]	wt % HFP		63
	mol % HFP		53
	% HFP as diads		15
inherent viscosity[d]			0.358
glass transition temperature	T_g/K[e]		311.5

[a] Pressure Chemical Co., Special Polystyrene Polymer, batch no. PS 50522. [b] By gel permeation chromatography (using 3M FC-75 fluorocarbon solvent at 353 K for amorphous TFE−HFP copolymer). [c] By fluorine NMR. [d] In 3M FC-75 fluorocarbon solvent at 298 K. [e] By differential scanning calorimetry, second heat at 10 K/min under N_2 purge.

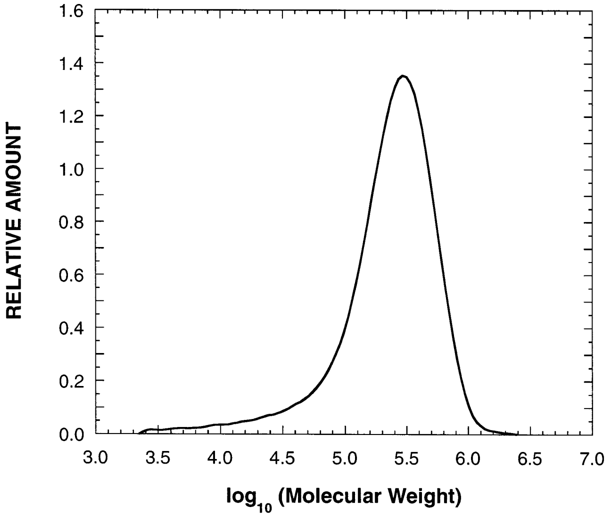

Figure 2. Molecular weight distribution (gel permeation chromatography) for the amorphous TFE−HFP copolymer.

Materials. Table 1 presents characterization data for the polymers used in this study. Polystyrene was obtained from the Pressure Chemical Co. (Pittsburgh, PA) and is believed to be the same batch of polymer used by Hadj Romdhane and Danner[12] for a similar experimental measurement validation as described below. The amorphous TFE−HFP copolymer was supplied by DuPont and was selected as representative of the various formulations under evaluation at the time of this work. Figure 2 shows the molecular weight distribution for this material.

The various "solutes" used for measurements with this polymer consist of the monomers, their dimers, and selected potential solvents of interest. Table 2 summarizes these materials, and a variety of functional groups are represented in the solute + polymer interactions for the selected components. The 3M PF series fluorinated solvents were analyzed by GC−mass spectrometry (MS) to determine their approximate compositions based on mass spectral databases developed within DuPont, and Table 3 summarizes these results. Further work to identify unknown isomers was not conducted, but this analysis was sufficient to confirm the identity of the primary constituents of each material and to confirm that each is a mixture of similar primarily perfluorinated alkanes. For each of these mixed solutes, the constituents were sufficiently alike so that only a single solute peak was detectable in the gas chromato-

Table 2. Description of Solutes

compound name	abbreviation	formula	molecular weight	normal boiling point/K	CAS no.	source
benzene	benzene	C6H6	78.11	353.2[c]	71-43-2	Aldrich
cyclohexane		C6H12	84.16	353.8[c]	110-82-7	Aldrich
cyclohexanone		C6H10(=O)	98.15	428.8[c]	108-94-1	Aldrich
1,1,1,2,3,4,4,5,5,5-decafluoropentane	Vertrel-XF	C5H2F10	252.06	328[a]	138495-42-8	DuPont
1,1-difluoroethane	F-152a	C2H4F2	66.05	248.2[c]	75-37-6	DuPont
1,1,2,2,3,4-hexafluoro-3,4-bis(trifluoromethyl) cyclobutane[f]	Vertrel-245	C6F12	300.05	318[a]	2994-71-0	DuPont
hexafluoroethane	F-116	C2F6	138.01	194.9[a]	76-16-4	DuPont
hexafluoropropylene	HFP	C3F6	150.02	244[a]	116-15-4	DuPont
hexane	hexane	C6H14	86.18	342.0[c]	110-54-3	Aldrich
octafluorocyclobutane	F-318	C4F8	200.03	267.2[a]	115-25-3	PCR Inc.[e]
perfluorobutane[f]	PF-5040[g]	C4F10	238.03	∼271[b]	355-25-9	3M
perfluoroheptane[f]	PF-5070[g]	C7F16	388.05	∼353[b]	86508-42-1	3M
perfluorohexane[f]	PF-5060[g]	C6F14	338.04		86508-42-1	3M
perfluoromethyl-morpholine[f]	PF-5052[g]	C5F11NO	299.04		86508-42-1	3M
perfluoropentane[f]	PF-5050[g]	C5F12	288.04	∼306[b]	86508-42-1	3M
perfluorooctane[f]	PF-5080[g]	C8F18	438.06	∼370[b]	86508-42-1	3M
tetrafluoroethene	TFE	C2F4	100.02	197.6[a]	116-14-3	DuPont
toluene	toluene	C7H8	92.14	383.8[c]	108-88-3	Aldrich
1,1,2-trichloro-1,2,2-trifluoroethane	F-113	C2F3Cl3	187.38	321[a]	76-13-1	DuPont
trifluoromethane	F-23	CHF3	70.01	191.1[c]	75-46-7	DuPont
2,2,4-trimethylpentane	isooctane	C8H18	114.23	372.4[d]	540-84-1	Aldrich

[a] DuPont MSDS. [b] 3M MSDS. [c] Reid, Prausnitz, and Poling (ref 19). [d] *Lange's Handbook of Chemistry* (ref 20). [e] Now Lancaster Synthesis, Ltd. (U.K.). [f] Nominal composition; mixture of isomers (see Table 3). [g] 3M Brand PF Series Performance Fluids.

Table 3. Analysis of 3M PF Series Solvents

PF solvent	principal components[a]	global formula	molecular weight	concentration/(area %)
PF-5040 (99.4% C4F10)	decafluoroisobutane	C4F10	238	82.9
	decafluorobutane	C4F10	238	16.5
	F-329	C4F9H	220	0.2
	FC-217ca	C3F7Cl	204	0.1
PF-5050 (96.8% C5F12)	dodecafluoropentane	C5F12	288	74.4
	dodecafluoroisopentane	C5F12	288	21.7
	unknown isomer	C5F12	288	0.4
	unknown isomer	C5F12	288	0.3
PF-5060 (98.1% C6F14)	unknown isomer	C6F14	338	59.5
	tetradecafluorohexane	C6F14	338	38.6
	dodecafluorocyclohexane	C6F12	300	0.5
	unknown isomer	C5F12	288	0.1
PF-5070 (85.8% C7F16)	unknown isomer	C7F16	388	57.2
	unknown isomer	C7F16	388	17.6
	unknown isomer	C7F16	388	11.0
	unknown isomer	C6F14	388	2.5
PF-5080 (94.9% C8F18)	unknown isomer	C8F18	438	56.4
	unknown isomer	C8F18	438	27.0
	unknown isomer	C8F18	438	7.1
	unknown isomer	C8F18	438	2.8
	unknown isomer	C8F18	438	1.6
PF-5052 (94.2% C5F11NO)	perfluoromorphyline	C5F11NO	299	94.2
	unknown isomer	C5F12	288	0.4
	unknown isomer	?	230	1.7
	unknown isomer	C6F14	338	1.5

[a] Analysis by gas chromatography (HP 6890) with FID quantification and mass spectrometer identification of components. Separation was accomplished on a 5% Krytox 143 hmw (6 m × 3.2 mm) 60/80 mesh Carbopack BHT column.

gram. The listed 3M fluorochemical PF-5080 was also used as the column preparation solvent as described below. All materials were used as received without further purification.

The solid supports Chromosorb W (Manville, 45/60 mesh, acid-washed, dimethyldichlorosilane treated) and Fluoropak 80 (40/60 mesh) were obtained from Alltech Associates. Chromosorb W-HP (100/120 mesh) support was obtained from Supelco. The Chromosorb W and W-HP supports are a diatomaceous earth material, and the Fluoropak is a powdered Teflon.

Selection of Solid Support. For the measurement of thermodynamic quantities by this inverse gas chromatographic technique where the solvent (i.e., the polymer) is spread on an "inert" solid support, one must consider the possible adsorption of the solute by residual uncoated surfaces of the support.[3] This question of solid support has been addressed by a number of researchers. For example, Newman and Prausnitz[7] state that diatomaceous-earth-based supports (e.g., Chromosorb W) give badly asymmetric peaks for polar solvents and show a dependence of retention time on sample size. They further state that powdered Teflon supports (e.g., Fluoropak 80) produce nearly symmetric peaks for both polar and nonpolar solvents and eliminate this dependence of retention time. However, Conder[16] studied Teflon as a chromatographic support in detail and concluded that adsorption by Teflon contributes substantially to the retention of a variety of both polar and nonpolar solutes, and thus Teflon does not fulfill the role as an ideal support for such gas chromatographic studies.

Table 4. Adsorption of Selected Solutes on Uncoated Solid Supports at 423 K

solute	specific retention volume (V_g) (cm^3/g of solid support) Chromosorb W	 Fluoropak-80
HFP	0.019	0.028
TFE	0.012	0.015
F-113	−0.019	0.073
Vertrel-245	−0.004	0.055[a]
hexane	−0.043	0.048
benzene	0.027	0.059
toluene	0.019	0.113
isooctane	0.019	0.086[a]
F-116	0.019	0.012
F-23	0.012	0.008
PF-5050	−0.012	0.068
PF-5052	−0.004	0.075
PF-5060	−0.004	0.098[a]
PF-5070	0.004	0.186[a]
PF-5080	0.012	0.363[a]
F-152A	0.043	0.018
F-318	0.046	0.041

[a] Tailing chromatographic peak.

A subsequent detailed study on this topic by Hadj Romdhane and Danner[12] included injection of a number of polar and nonpolar solutes on both Chromosorb W and Fluoropak 80 solid supports to determine the effect on peak symmetry and retention time. Their results indicate that surface adsorption of nonpolar solvents by the Fluoropak support was almost 10 times greater than adsorption by the Chromosorb material. For most of the polar solvents, however, Fluoropak gave less surface adsorption, superior peak symmetry, and no dependence of retention time on sample size.

Since Hadj Romdhane and Danner's study did not include perfluorinated compounds that were planned for the current study, similar measurements were conducted here to confirm these prior indications for the specific solutes of current interest. This evaluation was done by measuring the retention times of the various solutes injected into columns of uncoated Fluoropak 80 and Chromosorb W (6.4 mm o.d. × 0.9 mm wall × 0.25 m long 316 SS tubing; the support was packed between two approximately 0.1 m plugs of glass wool at the ends of the columns). These blank columns were first preconditioned by heating to 423 K overnight under a helium purge. Table 4 lists the resulting specific retention volumes for injection of the indicated samples versus that of nitrogen, which was used as an unadsorbing reference gas. The results indicate that several of the nonpolar solutes show significant adsorption on Fluoropak 80. Negligible interaction is seen for the solutes of interest on Chromosorb W; hence Chromosorb W was used for the experimental measurements in this work.

Preparation of Polymer-Coated Column Packing. The sample columns were prepared from 6.4 mm o.d. 316 SS tubing packed with Chromosorb W or Chromosorb W-HP (for the polystyrene column) coated with the polymer of interest as described below. The following method was used for coating the solid support with polymer. For each case, this technique successfully produced a free flowing "powder" and, presumably, an even coating on the support.

The coverage ratio is defined as the mass ratio of polymer to support in the column and is an important parameter in considering the main mechanisms for the sorption of solutes in using this gas chromatographic technique (i.e., surface adsorption versus bulk absorption). Schreiber et al.[9] have shown for polyethylene systems that measured results are independent of the coverage ratio when the ratio exceeds about 0.05. Therefore, a relatively high coverage ratio of approximately 0.13 to 0.18 was selected for the present measurements, and this effect was not examined further in this study.

To coat the selected support material with polymer, a weighed polymer sample was dissolved at an approximately 2 mass % concentration in an appropriate solvent at room temperature from several hours to overnight in a 500-mL round-bottomed flask. Methylene chloride was used as the solvent for the polystyrene standard polymer, and 3M Fluorinert PF-5080 was used for the TFE−HFP copolymer. The flask was mounted and rotated slowly on a Buchi rotary evaporator to promote complete dissolution. The support material was dried overnight in a vacuum oven at 393 K prior to use. When the polymer was completely dissolved in the solvent, a known mass of the dried support material was added to the flask, and the rotation at room temperature was resumed for 1 h. For subsequent flask rotation, a curved wire insert was devised that was inserted into the flask and mounted externally to a support stand. This wire insert effectively wiped the wall of the flask as it rotated to prevent agglomeration of the particles and their sticking to the glass wall during evaporation of the solvent. Chilled water was then supplied to the rotary evaporator condenser coil, and a slight vacuum was supplied to the effluent line. The flask was then heated to approximately (313 to 318) K in a water bath to produce a slow evaporation rate. The bath temperature was increased once the visible liquid had evaporated to ensure complete evaporation of the solvent. The flask was then removed from the rotary evaporator and placed in a vacuum oven at 388 K to dry to constant mass, typically overnight. The dried coated support was then sieved through a no. 45 mesh screen to produce a uniform free-flowing powder. This material was thoroughly mixed, and a sample was taken for subsequent thermogravimetric analysis (TGA) as described below.

Column Loading. The columns were prepared from 6.4 mm o.d. × 0.7 mm wall 316 SS tubing. One end of the column was plugged with glass wool (silane-treated Pyrex fiberglass) and a Swagelok cap, and then the coated support was poured into the column with occasional mechanical vibration or tapping throughout the length of the tubing to ensure tight packing. The filling end of the column was then similarly plugged with glass wool and a Swagelok cap. The tubing was then coiled to fit into the external oil bath of the apparatus. Once installed, the loaded column was heated under helium purge at 398 K for a minimum of 4 h to remove all volatile components prior to use for measurements.

The amount of polymer loaded in the column was determined by a combustion technique using TGA. Samples of the uncoated dried solid support, the original polymer, and the polymer-coated support were scanned at temperatures up to 1230 K, and the polymer loading was calculated from the TGA weight-loss traces. Table 5 summarizes details of the three columns used in this study.

Experimental Validation with Polystyrene. The experimental apparatus, techniques, and data reduction methods were validated by measuring and comparing the infinite dilution volatilities of several solute + polystyrene systems with published literature values. Specifically, measurements were taken using polystyrene coated on a Chromosorb W-HP substrate and compared with similar measurements reported by Hadj Romdhane and Danner.[12] As noted above, the polystyrene used for these measurements is believed to be from the same batch of polymer as

Table 5. Description of Chromatographic Columns

polymer	column no.	preparation solvent	solid support	polymer mass/g	polymer loading/(mass %)	coverage ratio	column length/m
polystyrene	PS	CH_2Cl_2	Chromosorb W-HP	2.007	12.19	0.139	3
amorphous TFE−HFP copolymer	I	PF-5080	Chromosorb W	1.839	11.47	0.130	3
amorphous TFE−HFP copolymer	II	PF-5080	Chromosorb W	4.989	15.53	0.184	6

Table 6. Measured Mass Fraction Activity Coefficients for Polystyrene Systems Compared with Literature Data

	cyclohexane		benzene		toluene		cyclohexanone	
	$T = 423$ K	$T = 448$ K	$T = 423$ K	$T = 448$ K	$T = 423$ K	$T = 448$ K	$T = 423$ K	$T = 448$ K
V_g/cm^3/g	10.5	7.1	16.4	10.9	28.6	17.2	70.4	40.6
P_1^s/bar[a]	5.53	8.84	5.81	9.37	2.75	4.69	0.87	1.61
M_1	84.16	84.16	78.11	78.11	92.14	92.14	98.15	98.15
V_1/cm^3/gmol[a]	130.5	137.2	106.9	112.2	125.0	130.3	118.9	122.9
B_{11}/cm^3/gmol[a]	−654.6	−562.5	−605.1	−529.3	−946.6	−810.2	−1389	−1190
γ_w^∞ (this work)	8.10	8.27	5.32	5.49	5.29	5.65	6.06	6.13
γ_w^∞ (literature data)[b]	10.1	8.61	5.69	5.62	5.67	5.63	6.07	6.05

[a] DIPPR Database (1997) (ref 17). [b] Hadj Romdhane and Danner (ref 12).

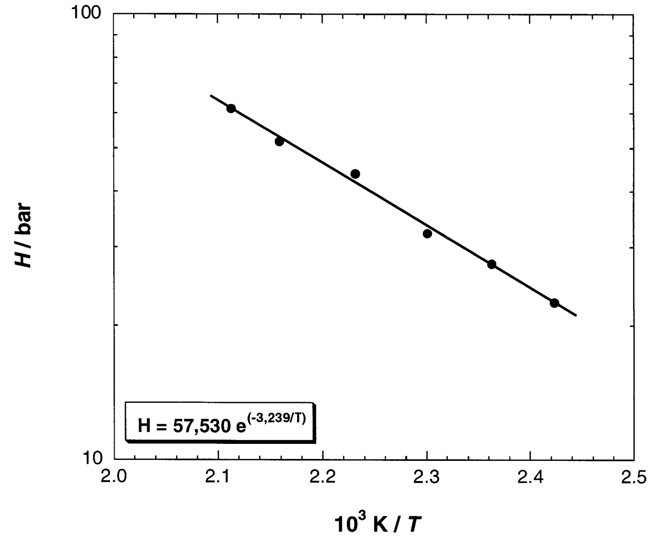

Figure 3. Temperature dependence of the mass fraction Henry's law coefficient for the benzene + polystyrene system. The solid line represents the correlation provided in the inset.

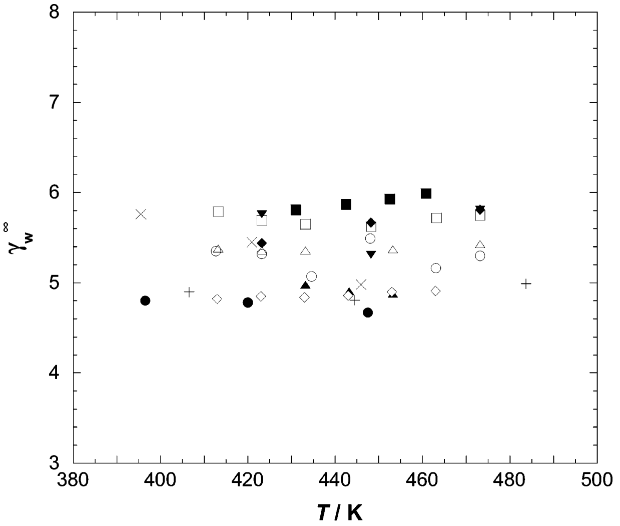

Figure 4. Comparison of the temperature dependence of the infinite dilution mass fraction activity coefficient (γ_w^∞) for the benzene + polystyrene system with literature data: (□) Hadj Romdhane and Danner (ref 12) (M_n = 86 700); (+) Covitz and King (ref 21) (M_n = 80 000); (●) Covitz and King (ref 21) (M_n = 96 200); (×) Covitz and King (ref 21) (M_n = 1 780 000); (▲) DiPaola-Baranyi and Guillet (ref 22) (M_n = 120 000); (♦) Newman and Prausnitz (ref 7) (M_n = 97 600); (▼) Lipatov and Nesterov (ref 23) (M_n = 190 000); (■) Inoue et al. (ref 24) (M_n = 1 800 000); (△) Galin and Rupprecht (ref 18) (M_n = 76 000); (◇) Schuster, Gräter, and Cantow (ref 25) (M_n = 53 700); (○) this work (M_n = 86 700).

that used in that comparison study. The experimental techniques and data reduction methods used for this comparison were essentially identical to those used in the subsequent measurements for the TFE−HFP copolymer.

Table 6 summarizes the results for four binaries of this polystyrene with cyclohexane, benzene, toluene, and cyclohexanone at 423 K and 448 K. The reported infinite dilution mass fraction activity coefficients were calculated from eq 5 using the indicated physical property data obtained from the DIPPR database.[17] The agreement is reasonably good (within 7%) for all values except the lower temperature cyclohexane result (within 20%). The reported data for this current work at that temperature were reproducible, and it is not clear why there is such a discrepancy at this one value. However, note that both the literature results and those of this work show only a modest temperature effect on the infinite dilution activity coefficient over this range for the three other components. This modest temperature dependence is also seen in the results reported for cyclohexane in this study, but not in the results reported by Hadj Romdhane and Danner.

For a more extensive comparison, the temperature range of measurements for the benzene + polystyrene system was expanded to cover six points ranging from (413 to 473) K. Figure 3 presents these results plotted to show the temperature dependence of the Henry's law coefficient (eq 1) for this system. As illustrated, the data show little scatter over this range, and the indicated fit to an Arrhenius temperature dependency is quite good. Figure 4 shows these results in the form of the infinite dilution mass fraction activity coefficients calculated from eq 5 and compared with literature values from a number of reported measurements for this system. The data of the current study are in good agreement with those reported by Hadj Romdhane and Danner,[12] Newman and Prausnitz,[7] and Galin and Rupprecht.[18] However, there is clearly significant scatter in the results of the various studies reported in Figure 4, which is indicative of the level of experimental error that can occur in such measurements using this technique.

On the basis of the reasonable agreement between the current measurements and the literature results presented above, the experimental equipment and methods used in

Table 7. Mass Fraction Henry's Law Coefficients for Various Solvents in Amorphous TFE−HFP Copolymer

solute	correlation	correlation coefficient	T/K	H/bar measd	H/bar fitted
TFE	$H = 37620 \exp(-1387/T)$	0.9895	321.5	472	503
			332.2	554	578
			357.2	835	774
			411.9	1459	1300
			466.5	1935	1920
			511.1	2280	2490
HFP	$H = 24920 \exp(-1631/T)$	0.9918	321.5	173	156
			332.3	155	184
			357.1	258	259
			411.9	540	475
			466.4	769	755
			511.1	951	1020
F-318	$H = 23850 \exp(-1890/T)$	0.9986	357.1	122	120
			412.0	233	243
			466.4	430	414
			511.1	585	591
Vertrel-245	$H = 17720 \exp(-2262/T)$	0.9967	357.1	32.3	31.4
			411.8	70.8	72.9
			466.5	132	139
			511.2	224	212
F-116	$H = 17010 \exp(-1054/T)$	0.9970	332.5	676	714
			357.2	942	889
			412.0	1330	1320
			466.5	1800	1780
			511.1	2100	2160
PF-5040	$H = 10440 \exp(-1595/T)$	0.9984	357.2	117	120
			412.0	229	217
			466.4	341	341
			511.1	450	461
PF-5050	$H = 19870 \exp(-2142/T)$	0.9950	332.5	34.0	31.6
			357.1	46.9	49.3
			412.0	103	110
			466.5	190	201
			511.0	327	300
PF-5060	$H = 34310 \exp(-2674/T)$	0.9979	332.4	11.2	11.0
			357.2	19.7	19.2
			412.0	49.6	52.1
			466.5	106	111
			511.1	195	183
PF-5070	$H = 71470 \exp(-3265/T)$	1.0000	332.4	3.70	3.87
			357.2	8.07	7.65
			412.0	26.0	25.8
			466.4	64.2	65.1
			511.2	120	120
PF-5080	$H = 125800 \exp(-3778/T)$	0.9999	332.3	1.33	1.45
			357.1	3.48	3.19
			412.0	13.8	13.1
			466.5	37.4	38.2
			511.1	75.3	77.5
hexane	$H = 124100 \exp(-2374/T)$	0.9978	321.5	79.1	77.0
			357.2	146	161
			411.9	439	389
			466.5	765	765
			511.1	1140	1190
benzene	$H = 93620 \exp(-2463/T)$	0.9918	332.5	52.6	56.7
			357.2	92.5	94.7
			411.9	300	237
			466.5	446	477
			511.2	704	756
isooctane	$H = 63320 \exp(-2504/T)$	0.9986	332.5	33.7	33.9
			357.2	57.8	57.1
			412.0	147	145
			466.5	281	295
			511.1	487	472
toluene	$H = 117000 \exp(-2817/T)$	0.9943	321.5	16.8	18.3
			357.2	43.7	43.9
			411.8	158	125
			466.4	262	279
			511.2	433	473
F-23	$H = 21030 \exp(-831.7/T)$	0.9852	332.3	1790	1720
			357.2	1940	2050
			412.0	2740	2790
			466.4	3810	3530
			511.0	3970	4130
F-152a	$H = 70580 \exp(-1620/T)$	0.9341	321.5	390	457
			357.1	804	755
			411.8	1980	1380
			466.3	1800	2190
			511.1	2780	2960
Vertrel-XF	$H = 65360 \exp(-2741/T)$	0.9998	332.4	15.8	17.1
			357.2	32.9	30.4
			411.8	87.2	84.0
			466.5	180	183
			511.1	299	306
F-113	$H = 30270 \exp(-2407/T)$	0.9999	332.4	20.6	21.7
			357.1	38.1	35.8
			412.0	88.4	87.8
			466.5	172	174
			511.2	271	273
PF-5052	$H = 24620 \exp(-2480/T)$	0.9984	332.3	14.8	14.1
			357.2	23.4	23.8
			412.1	55.9	59.9
			466.5	119	121
			511.1	204	192

the subsequent measurements for the amorphous TFE−HFP copolymer systems were considered to be valid.

Results and Discussion

Table 7 summarizes the results for the solute + TFE−HFP copolymer systems measured in this study. The measurements are presented as mass fraction Henry's law coefficients calculated from eq 1. The measured data were smoothed by fitting the experimental results to an Arrhenius relationship given by the natural logarithm of the Henry's law coefficient as a function of the inverse absolute temperature. Table 7 includes these correlations and compares the experimental data with the calculated values.

Figures 5−8 present plots of these data and correlated results. Figure 5 summarizes results for the monomers (TFE and HFP) and their associated dimers. Figure 6 presents similar results for several perfluorinated alkanes being considered as process solvents, and Figure 7 shows comparable data for representative hydrocarbon and hydrofluorocarbon solvents. Figure 8 presents results for the chlorofluorocarbon F-113 and PF-5052.

Data reported in Table 7 and Figures 5−8 represent averaged results from replicate measurements using two different chromatographic columns (columns I and II of Table 5). The data show good repeatability for these measurements and smooth trends with relatively little scatter over the measured temperature range.

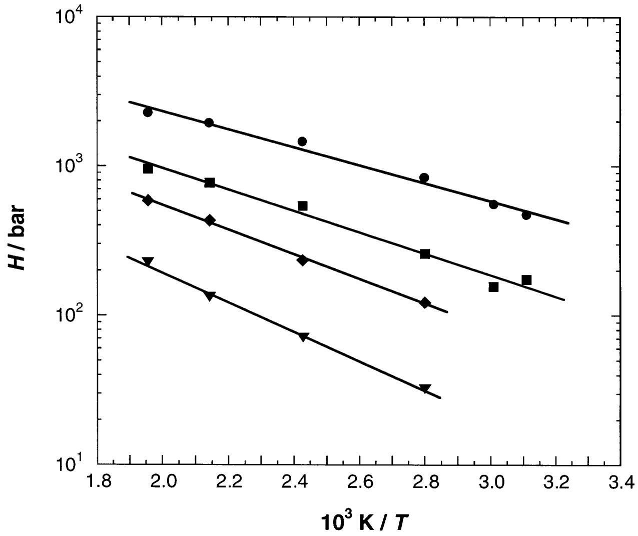

Figure 5. Mass fraction Henry's law coefficients for TFE, HFP, and associated dimers in amorphous TFE−HFP copolymer: (●) TFE; (■) HFP; (♦) F-318 (TFE dimer); (▼) Vertrel-245 (HFP dimer). The solid lines represent the correlations provided in Table 7.

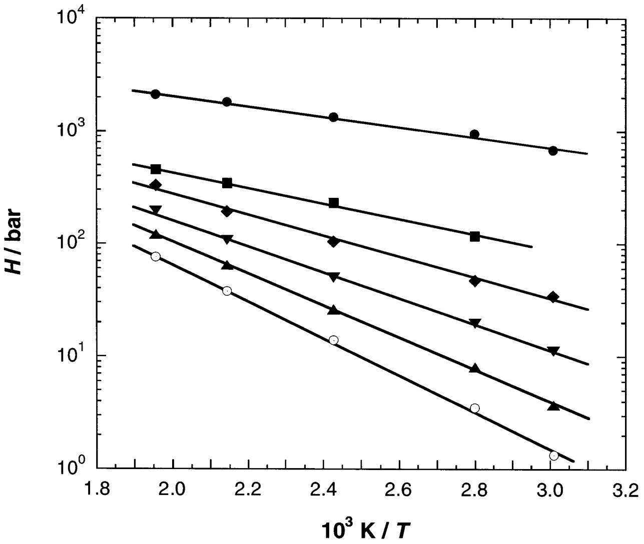

Figure 6. Mass fraction Henry's law coefficients for selected perfluoroalkane solvents in amorphous TFE−HFP copolymer: (●) F-116; (■) PF-5040; (♦) PF-5050; (▼) PF-5060; (▲) PF-5070; (⊙) PF-5080. The solid lines represent the correlations provided in Table 7.

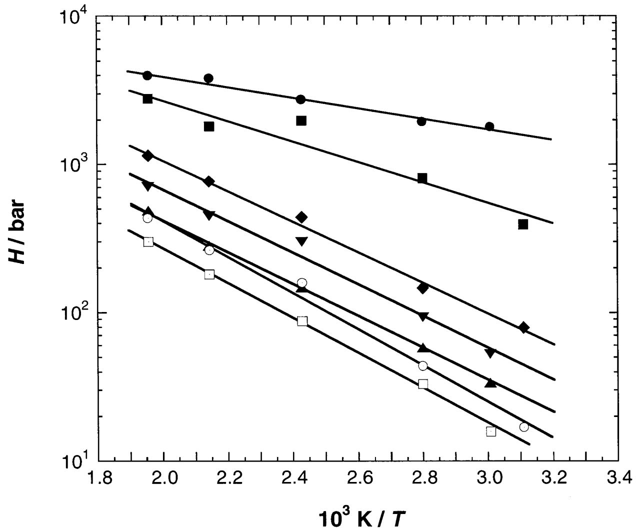

Figure 7. Mass fraction Henry's law coefficients for selected hydrocarbons and hydrofluorocarbons in amorphous TFE−HFP copolymer: (●) F-23; (■) F-152a; (♦) hexane; (▼) benzene; (▲) isooctane; (⊙) toluene; (⊡) Vertrel-XF. The solid lines represent the correlations provided in Table 7.

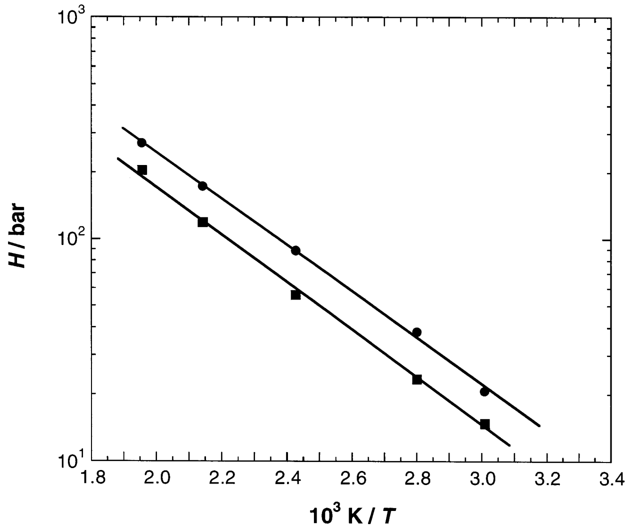

Figure 8. Mass fraction Henry's law coefficients for Freon-113 and PF-5052 in amorphous TFE−HFP copolymer: (●) F-113; (■) PF-5052. The solid lines represent the correlations provided in Table 7.

As evidenced by the lower Henry's law coefficient, Figure 5 indicates that stronger interactions exist between this copolymer and the HFP monomer than with the TFE monomer. Likewise, both dimers interact more strongly with the copolymer than either of the monomers, and in the same respective order. Similar variation in the strength of solute + polymer interactions is illustrated in Figures 6−8. For example, Figure 6 shows an increase in the strength of these interactions with increasing carbon number for the illustrated range of perfluoroalkanes. Similarly, Figure 7 shows stronger interactions for isooctane, toluene, and Vertrel-XF than for the solvents F-23, F-152a, hexane, and benzene.

In practical applications, the measured Henry's law coefficients can be used to estimate the solubility of residual monomers, their dimers, and various process solvents in the amorphous TFE−HFP copolymer as a function of the polymer temperature using Henry's law. These estimates are important for process development applications where suitable conditions must be specified for the economical recovery of these components from the finished polymer. By Henry's law, those components exhibiting stronger interactions with the polymer (i.e., lower Henry's law coefficients) will require more extreme process conditions (e.g., higher temperatures or lower pressures) to adequately isolate the component from the polymer. Such data can thus be used to aid the rational selection of potential process solvents by evaluating the ease of solvent recovery in downstream separation processes.

Conclusions

Inverse gas chromatography is an experimentally convenient method for determining thermodynamic interaction data for solute + polymer systems at infinite dilution. In practical applications, such data can be used to determine suitable conditions for the economical recovery of these components from the polymer.

Henry's law coefficients have been measured using a standard inverse gas chromatographic technique for the monomers, their dimers, and a number of potential process solvents in an amorphous copolymer of TFE and HFP. The specific amorphous TFE−HFP copolymer used for these measurements was characterized by fluorine NMR as consisting of 53 mol % HFP and 47 mol % TFE with 15% of the HFP as diads. A number-average molecular weight of 104 000 with a polydispersity of 2.81 was determined by gel permeation chromatography analysis. A total of 19 binary systems were measured for this polymer at 4−6 temperatures over the range of (321 to 511) K. The experimental data are correlated by fitting with an Arrhenius temperature dependency.

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