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Thermodynamics of Sorption in an Amorphous Perfluorinated Rubber Studied by Inverse Gas Chromatography

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ABSTRACT: The work is aimed to further investigate thermodynamics of sorption of organic vapors in perfluorinated polymers. Amorphous perfluorinated random copolymer of 50.7 mol % tetrafluoroethylene and 49.3 mol % perfluoromethylvinyl ether, poly(TFE−PMVE), was studied using the inverse gas chromatography method. As solutes, several hydrocarbons and fluorocarbons of different classes were studied, namely, *n*-alkanes C_7−C_{10}, benzene and toluene, methylcyclohexane, *n*-perfluoroalkanes C_6 and C_8, perfluoromethylcyclohexane, perfluorinated benzene, and toluene. In addition, partially fluorinated toluene derivatives were investigated. It was shown that solubility coefficients *S* of fluorocarbons in this rubbery polymer are significantly higher than those of their hydrocarbon analogues. Correlations of the type $\ln S = A + BT_c^2$, where T_c is the critical temperature of the solutes, were demonstrated for both hydrocarbons and fluorocarbons; however, the curve for fluorocarbons is located above that of hydrocarbons. Therefore, in this regard, the behavior of perfluorinated rubber is analogous to the amorphous glassy perfluorinated polymers studied earlier. Hydrocarbons and fluorocarbons also reveal significant differences in other thermodynamic parameters of sorption in poly(TFE−PMVE): enthalpies of sorption, activity coefficients, partial molar enthalpies of mixing, and Flory−Huggins parameters.

1. Introduction

Amorphous perfluorinated polymers are distinguished by interesting physicochemical properties as materials for gas separation membranes. Some of them have very high permeability for gases and liquids[1−3] and large free volume.[4,5] All perfluorinated polymers (both amorphous and semicrystalline) have extremely good chemical stability,[6] reduced surface energy,[7] and unusually low activation energy of diffusion.[8,9]

Recently, interesting phenomena were demonstrated for sorption of fluorocarbons and hydrocarbons in amorphous Teflon AF: Fluorocarbons C_1−C_7 have systematically higher solubility coefficients *S* as compared to what can be expected from correlations of *S* with the critical temperature of other solutes including hydrocarbons.[10−13] On the other hand, solubility coefficients of fluorocarbons in common hydrocarbon based glassy and rubbery polymers are reduced as compared to hydrocarbon solutes with corresponding critical temperatures.[14−17]

Interestingly, the first observation of this effect could be made but was not properly interpreted as early as in 1994 in the study of gas sorption of partly fluorinated metathesis polynorbornenes: poly[5,5-difluoro-6,6-bis(trifluoromethylnorbornene] and poly[5,5,6-trifluoro-6-(heptafluoropropoxy)norbornene].[18] It was found that in these polymers the sorption isotherms of ethane are located below than those of carbon dioxide while in hydrocarbon-based polymers the order of these isotherms is opposite. However, it was ascribed to higher solubility of CO_2 in fluorine-containing polymers.

A summary of the studies of solubility of fluorocarbons and hydrocarbons in perfluorinated and hydrogen-based polymers is given in Table 1. Since gas and vapor sorption and diffusion phenomena are different in polymers below and above their corresponding glass transition temperatures, T_g, it is quite desirable to have information on sorption in amorphous polymers with T_g below room temperature. Homopolymers and copolymers of tetrafluoroethylene and hexafluoropropylene are not suited as objects of such investigation because of their semicrystalline nature.

Table 1. Polymers with Peculiarities of Solubility of Fluorocarbons and Hydrocarbons

chemical structure	glassy	effect	rubbery	effect
PF polymers	amorphous Teflon AF2400[10] ($T_g = 240$ °C) amorphous Teflon AF1600[12] ($T_g = 160$ °C)	enhanced solubility of FC	?	?
HC polymers	poly(1-trimethylsilyl-1-propyne)[16] ($T_g > 300$ °C)	reduced solubility of FC	poly(dimethylsiloxane)[17] ($T_g = -123$ °C)	reduced solubility of FC

An amorphous random copolymer of 50.7 mol % tetrafluoroethylene and 49.3 mol % perfluoromethylvinyl ether, poly(TFE−PMVE), is an interesting candidate for such study. Investigation of gas and vapor sorption of hydrocarbons and fluorocarbons in this polymer was undertaken in several laboratories. The first results on sorption of gaseous C_1−C_3 hydrocarbons and fluorocarbons and C_5−C_6 hydrocarbons have been reported by Prabhakar et al.[19]

In this work we present the results of the investigation of sorption thermodynamics in this copolymer using the inverse gas chromatography method. Measurements were performed for a wide range of solutes including aromatic and aliphatic fluorocarbons C_6−C_8, hydrocarbons C_6−C_{10}, and solutes containing both hydrogen and fluorine atoms.

2. Background

The inverse gas chromatography (IGC) of polymers is based on the theory of equilibrium gas chromatography.[20−22] In the IGC method, retention times of sorbed (t_r) and "nonsorbed" (t_a) components are measured. The value t_a that corresponds to

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virtually weakly sorbed component (e.g., air or methane) is needed to account for the dead volume of the chromatograph. Using the values t_r and t_a, the net retention volume V_N can be found:

$$V_N = (t_r - t_a)F_c {J_2}^3 \frac{273.2}{T_{col}} \tag{1}$$

where F_c is the flux of gas carrier (cm^3/s), ${J_2}^3$ is the correction for pressure drop in the column,[23] and T_{col} (°K) is the temperature of the experiment.

After accounting for the mass of the polymer in the column, the specific retention volume V_g can be calculated:

$$V_g = \frac{V_N}{w_L} \tag{2}$$

where w_L (g) is the mass of polymeric phase in the column.

The specific retention volume can be related to Henry's distribution constant K

$$V_g = \frac{K}{\rho} \tag{3}$$

where ρ is the polymer density (g/cm^3). Hence, V_g can be regarded as a physicochemical parameter that characterizes the equilibrium in the solute−polymer system tested.

Different thermodynamic properties of gas (vapor)−polymer system can be calculated. Thus, Kawakami et al.[24] proposed IGC for determination of the infinite dilution solubility coefficient which accounts for the nonideality of the vapor phase:

$$S = \frac{1}{p^0}\rho V_g \exp\left(\frac{2B_{11} - V_1}{RT} p_0 {J_3}^4\right) \tag{4}$$

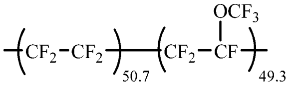
Here, $p^0 = 1$ atm is the standard value, the second virial coefficient B_{11} (cm^3/mol) and molar volume V_1 (cm^3/mol) of solutes can be calculated as recommended by Reid and Sherwood,[25] p_0 (Pa) is the inlet pressure in the column, and ${J_3}^4$ is the correction for pressure drop in the column.

The temperature dependence of S allows a determination of enthalpy of sorption ΔH_s:

$$S = S_0 \exp\left(-\frac{\Delta H_s}{RT}\right) \tag{5}$$

Another thermodynamic parameter that can be found via the specific retention volume is the reduced activity coefficient at infinite dilution:[26]

$$\ln\left(\frac{a_1}{w_1}\right)^\infty = \ln\left(\frac{273R}{V_g p_1^0 M_1}\right) - \frac{p_1^0}{RT}(B_{11} - V_1) \tag{6}$$



$$-\!\left(CF_2-CF_2\right)_{50.7}\!-\!\left(CF_2-\overset{OCF_3}{\overset{|}{CF}}\right)_{49.3}\!-$$

Figure 1. Structure of poly(TFE/PMVE).

where p_1^0 is the vapor pressure of the solute (Pa) at the experimental temperature T and M_1 (g/mol) is the molecular mass of the solute. Using the activity coefficient, it is possible to find partial molar free energy ΔG_m (kJ/mol), enthalpy ΔH_m (kJ/mol), and entropy ΔS_m (J/(mol K)) of mixing:

$$\Delta G_m = RT \ln\left(\frac{a_1}{w_1}\right)^\infty \tag{7a}$$

$$\Delta H_m = R\frac{\partial \ln\left(\frac{a_1}{w_1}\right)^\infty}{\partial(1/T)} \tag{7b}$$

$$\Delta S_m = \frac{\Delta H_m - \Delta G_m}{T} \tag{7c}$$

The process of solute vapor dissolution in a polymer can be described by a sequence of two stages: the condensation of vapors with the formation of a liquid phase followed by the mixing of this phase with the polymer to yield an infinitely dilute solution. Therefore, a change in the thermodynamic potentials (and partial molar enthalpy of mixing in particular) can be represented approximately as

$$\Delta H_m = \Delta H_s - \Delta H_c \tag{8}$$

where ΔH_c is the enthalpy of condensation of the solute. The enthalpy of condensation can be found at standard temperatures[27] or after accounting its temperature dependence.[25]

The Flory−Huggins parameter, χ_{12}, which characterizes thermodynamic interactions between the polymer and the solute, can be determined using IGC. In the conditions of infinite dilution and assuming sufficiently large molecular mass of the polymer, χ_{12} can be expressed by the formula[26]

$$\chi_{12} = \ln\left(\frac{273 v_2}{p_1^0 V_g V_1}\right) - 1 - \frac{p_1^0}{RT}(B_{11} - V_1) \tag{9}$$

where v_2 (cm^3/g) is the specific volume of the polymer.

On the basis of the Flory−Huggins model and Hildebrand−Scatchard solution theory, DiPaola-Baranyi and Guillet[28] proposed a method for the estimation of polymer solubility parameter δ_2. A treatment of the equation

$$\frac{{\delta_1}^2}{RT} - \frac{\chi_{12}}{V_1} = \frac{2\delta_2}{RT}\delta_1 - \frac{{\delta_2}^2}{RT} \tag{10}$$

where δ_1 (J/cm^3)$^{1/2}$ is the solubility parameter of the solutes, permits the estimation of δ_2 via either the slope or the intercept at the vertical axis in the coordinates (${\delta_1}^2/RT - \chi_{12}/V_1$) vs δ_1.

All these possibilities of IGC in the infinite dilution limit were examined in this work.

3. Experimental Section

3.1. Materials. Poly(TFE/PMVE) was kindly provided by DuPont Performance Elastomers, L.L.C. (Wilmington, DE). The chemical structure of this amorphous perfluoroelastomer is shown in Figure 1. This random copolymer of TFE and PMVE was prepared by continuous emulsion polymerization by simultaneously feeding a gaseous mixture consisting of TFE (44.2 g/h) and PMVE (83.2 g/h) and an aqueous solution (243 mL/h) containing 0.91 g/L of ammonium persulfate, 6.17 g/L of disodium phosphate heptahydrate, and 50.62 g/L of ammonium perfluorooctanoate to a 1 L, mechanically stirred autoclave. The temperature of the reaction was maintained at 85 °C and the pressure at 4.1 MPa (600 psi). The polymer emulsion was removed continuously by means of a letdown valve, and the unreacted monomers were vented. The emulsion from 24 h of operation was collected, and the polymer was isolated by first diluting the emulsion with 8 volumes of deionized water per volume of emulsion at a temperature of 60 °C and then adding a solution of 75 g/L of magnesium sulfate heptahydrate to the diluted emulsion at the rate of 0.3 volume of the magnesium sulfate solution per volume of emulsion. After stirring for 1 h at 60 °C, the coagulated polymer crumb was filtered, washed in deionized water for 30 min at 45 °C, filtered again, and dried in an air oven for 48 h at 70 °C. The polymer yield was 3.7 kg. The composition of the polymer, as determined by FTIR, was 50.7 mol % TFE and 49.3 mol % PMVE. The polymer's inherent viscosity was 0.65 dL/g, as measured in a solution of 0.1 g of polymer in 100 g of a solvent mixture consisting of 60/40/3 volume ratio of heptafluoro-2,2,3-trichlorobutane, perfluoro(butyltetrahydrofuran), and ethylene glycol dimethyl ether at 30 °C.

The glass transition temperature of this polymer is −8 °C as measured by a differential scanning calorimeter at a heating rate of 20 °C/min. The density of the polymer determined by the hydrostatic weighing method (liquid-phase 2-propanol) was found to be 2.02 ± 0.04 g/cm^3.

All the solutes studied had a purity not less than 98%. Only peak retention time was measured in the chromatographic experiments.

3.2. Chromatographic Measurements. Large pore solid carrier Inerton AW, with surface area about 0.5 m^2/g and a particle size of 0.16−0.20 mm, was used for coating the perfluorinated rubber. The deposition of poly(TFE/PMVE) was performed from a 5 mass % solution in the commercial solvent PF5060 (*n*-perfluorohexane, 3M Co., Minneapolis, MN). Slow evaporation of the solvent was carried out at atmospheric pressure and 30−35 °C in a rotary evaporator. Then the chromatographic phase was dried in a vacuum to constant weight. On the basis of weight loss determined by back-extraction, the concentration of the polymer phase on the solid carrier was 3.0 ± 0.5 mass %. This corresponds to the mean thickness of the polymer layer of ~500 nm. The measurements in the range 45−90 °C were performed using a LKhM-8MD chromatograph with thermal conductivity detector and a stainless steel column with the length 3 m and inner diameter 3 mm. The vapor samples were introduced with a syringe, using a sample size of about 1 μmol. The temperature of the sample evaporator was kept at 200 °C in all the experiments. Helium served as a gas carrier, and air peak was used for estimation of t_a. To introduce the corrections into eqs 1, 4, 6, and 9, the inlet pressure was checked using a high-sensitivity manometer, while the outlet pressure was taken as atmospheric.

A necessary step in a study of equilibrium chromatography is an estimation of the range of gas carrier flow rate with no diffusion limitations at different temperatures, based on the determination of specific retention volume as a function of gas flow rate F_c.[29] The flow rate in the experiments must be less than a certain limiting value such that there will be no dependence of V_g on F_c. An example at 45 °C is shown in Figure 2. It is seen that the equilibrium regime of dynamic sorption is attained at flow rate 5−10 cm^3/min, so this flow rate was used in the experiments at this and higher temperatures. Retention times t_r did not depend on the size of injected sample having the order of 1 μmol. This means that the thermodynamic parameters determined corresponded to the infinite dilution conditions.[29] Experimental errors were estimated using the Student coefficients with the confidence probability of 0.95.

Partial vapor pressures of the solutes were found according to the Antoine equation[30] and/or the equation $\ln P_{VP} = A \ln T + B/T + C + DT^2$, as calculated using the KDB[31] database.

The temperature dependence of the polymer density or specific volume has been reported by Prabhakar et al.[19] based on the experimental values obtained by Dr. F. Briatico (Polytechnic of Milan) and kindly provided to us. The original experimental data were approximated by the linear function $\rho(t) = A + Bt$, where t is the temperature (°C) and $\rho(t)$ is expressed in g/cm^3: $A = 2.054$ g/cm^3 and $B = -1.79 \times 10^{-3}$ g/(cm^3 K).

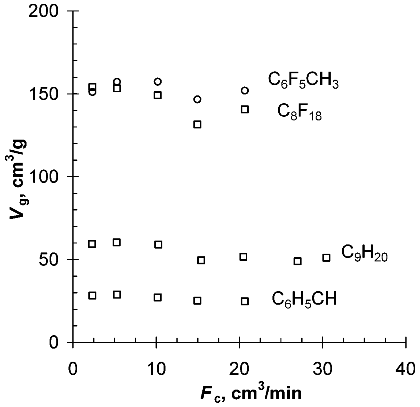


Figure 2. Effects of the gas carrier flow rate F_c on the specific retention volumes V_g of several solutes at 45 °C.

4. Results and Discussion

A set of carefully selected solutes was used in this study. They included *n*-alkanes C_7-C_{10}, aromatic hydrocarbons (benzene and toluene), methylcyclohexane, *n*-perfluoroalkanes C_6 and C_8, perfluoromethylcyclohexane, perfluorinated benzene and toluene, and toluene derivatives containing both H and F atoms: 4-fluorotoluene and 2,3,4,5,6-pentafluorotoluene.

4.1. Solubility Coefficients. Figure 3 shows the retention diagram, that is, the dependence of ln V_g vs reciprocal temperature. For all the solutes, the dependencies are linear. This means that no phase transitions occur in the temperature range studied, and the enthalpy of sorption is temperature-independent. The V_g values for the fluorocarbons are markedly larger than those of their hydrocarbon analogues. An examination of the figure indicates that the slopes of the dependences are steeper for fluorocarbons than those for hydrocarbons of different classes (e.g., benzene, *n*-heptane, methylcyclohexane). This point will be discussed in a more quantitative manner later in this paper.

Using eq 4 and dilatometric data reported by Prabhakar et al.,[19] the solubility coefficients S were calculated. It is well-known that the S values correlate with measures of gas condensability of solutes such as boiling point T_b, critical temperatures T_c, and Lennard-Jones energy parameter ϵ/k.[32,33] Since all these three parameters are linearly interrelated, these correlations are intrinsically similar. When a set of solutes is characterized by a relatively narrow range of variation of condensability, linear correlations are usually observed, for example:

$$\log S = a + bT_c \tag{11}$$

However, for larger sets of solutes, the data are better fitted by a nonlinear correlation of the type

$$\log S = a' + b'(T_c)^2 \tag{12}$$

This type of correlation has been demonstrated for both rubbery and glassy polymers.[34−38]

Figure 4 shows the correlation of the solubility coefficients S at 35 °C of various hydrocarbons and fluorocarbons studied in this work. For comparison, the results reported by Prabhakar et al.[19] for alkanes and fluoroalkanes C_1-C_3, *n*-alkanes, and cycloalcanes C_5-C_6 are also presented. The data obtained by

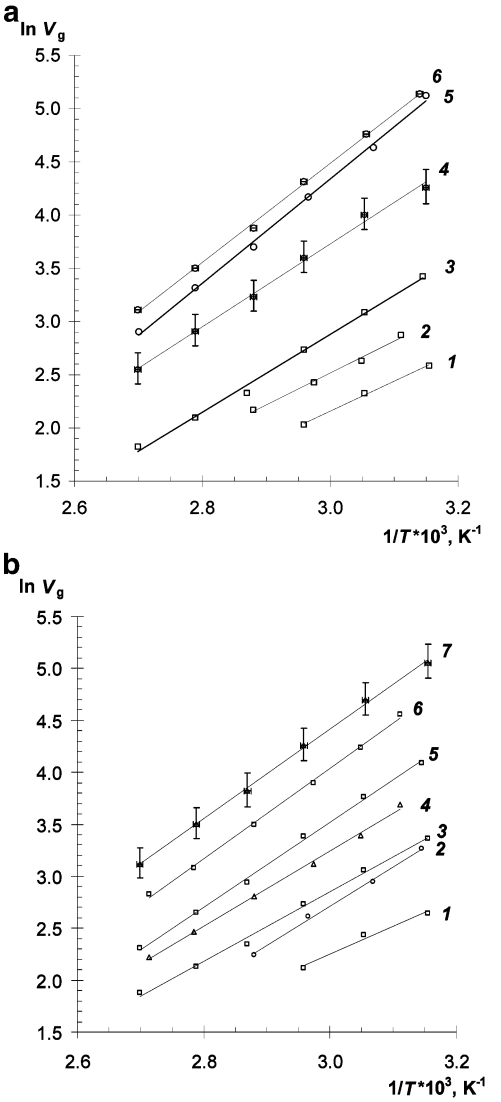


Figure 3. Retention diagram of several hydrocarbon and fluorocarbon solutes in poly(TFE-PMVE): (a) 1, benzene; 2, methylcyclohexane; 3, *n*-octane; 4, perfluorobenzene; 5, *n*-perfluorooctane; 6, perfluorotoluene; (b) 1, *n*-heptane; 2, *n*-perfluorohexane; 3, toluene; 4, 4-fluorotoluene; 5, *n*-nonane; 6, *n*-decane; 7, 1,2,3,4,5-pentafluorotoluene. The data for perfluoromethylcyclohexane overlap those of *n*-nonane, so for clarity the former is not shown in this figure.

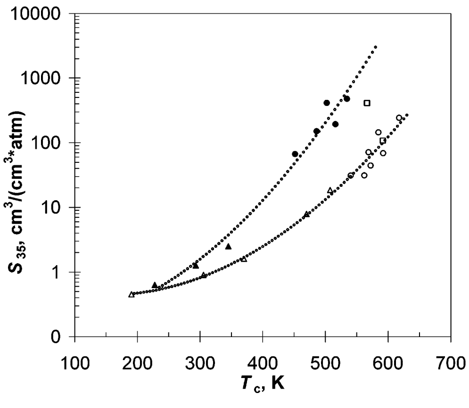


Figure 4. Correlation of the infinite dilution solubility coefficients *S* of fluorocarbons and hydrocarbons in poly(TFE/PMVE) with solute critical temperature T_c at 35 °C: filled points, fluorocarbons; open points, hydrocarbons; squares, partly fluorinated hydrocarbons; triangles are the data from ref 19.

IGC were subjected to short linear extrapolation to this temperature. Several conclusions can be made from this plot.

Table 2. Infinite Dilution Solubility Coefficients *S*, cm^3 (STP)/cm^3 atm of Fluorocarbons (FC) and Their Hydrocarbon (HC) Analogues at 45 °C

FC	*S*	HC	*S*
C_8F_{18}	271 ± 45	C_8H_{18}	50 ± 7
$C_6F_{11}CF_3$	109 ± 16	$C_6H_{11}CH_3$	30 ± 5
C_6F_6	125 ± 20	C_6H_6	24 ± 4
$C_6F_5CF_3$	290 ± 45	$C_6H_5CH_3$	50 ± 8

Table 3. Solubility of Alkanes and Fluoroalkanes C_1-C_3 (Bunsen Coefficients, cm^3 (STP)/cm^3 atm) in Hydrocarbon and Fluorocarbon Solvents

gas	cyclohexane	benzene	$N(C_3F_7)_3$	gas	cyclohexane	benzene	$N(C_3F_7)_3$
CH_4[37]	0.68	0.52	0.44	CF_4[40]	0.21	0.14	0.94
C_2H_6[38]	5.0	3.8	2.2	C_2F_6[40]	0.51	0.27	3.1
C_3H_8[39]	21.9	15.0		C_3F_8[40]	1.3	0.61	

1. The dependence $S(T_c)$ is strongly nonlinear and can be approximated by a parabola for both hydrocarbons and fluorocarbons, in agreement with the previous results.[10,12,34−36] Separate dependences $S(T_c)$ are observed for hydrocarbons and fluorocarbons.

2. Solubility coefficients of hydrocarbons in perfluorinated rubber are markedly lower than those of fluorocarbons. Solubility coefficients of the compounds containing both C−H and C−F bonds (partly fluorinated toluenes) have intermediate values. The difference between solubility coefficients of fluorocarbons and hydrocarbons increases with the molecular weight of the solutes. The difference is marginal for compounds C_1-C_3 but increases to 1 order of magnitude for compounds C_6-C_8. This result is consistent with the observation made earlier for glassy amorphous Teflon 1600.[12] Similar assumptions about the differences of the solubility of hydrocarbons and fluorocarbons were made more recently as well.[19]

As an additional illustration, Table 2 shows strong differences in the solubility coefficients of fluorocarbons of different classes (aliphatic, cycloaliphatic, aromatic) and their hydrocarbon analogues.

Therefore, the results of the present work fill the gap shown in Table 1 and indicate that enhanced solubility of fluorocarbons (or reduced solubility of hydrocarbons) is characteristic for the amorphous perfluorinated rubber studied.

Abundant data are available on solubility of fluorocarbons in low molecular mass hydrocarbon and fluorocarbon solvents as well as for hydrocarbons in the same two groups of solvents.[37−40] Some of these data are shown and examined in Table 3. The table indicates that hydrocarbon gases have a lower solubility in the fluorocarbon solvent tri(perfluoropropyl)amine in comparison to corresponding fluorocarbons with the same number of carbon atoms. For example, solubility of CH_4 is lower than that of CF_4 by a factor of about 2. Similar effects are observed for the other perfluorinated solvents. On the other hand, solubility of hydrocarbons in hydrogenated solvents is much higher than that of fluorocarbons (e.g., solubility of C_3H_8 and C_3F_8). It means that the effects of increased solubility of fluorocarbons in perfluorinated polymers observed by us and by Prabhakar et al.[19] have nothing to do with polymer state of these "solvents" and must be ascribed to point interactions between solutes and solvents. Interestingly, in these cases too the differences are greater for larger solutes, as has been noted in ref 14.

4.2. Enthalpy of Sorption and Partial Molar Thermodynamic Parameters. The temperature dependences of *S* were used for finding the enthalpies of sorption ΔH_s, which are presented in Table 4. It is seen that sorption of fluorocarbons in poly(TFE/PMVE) is characterized by noticeably more

Table 4. Enthalpy of Sorption in Poly(TFE−PMVE)

solute	ΔH_s, kJ/mol
n-heptane	−22.4 ± 1.0
n-octane	−30.4 ± 0.3
n-nonane	−33.9 ± 0.2
n-decane	−36.1 ± 0.3
methylcyclohexane	−24.9 ± 0.5
benzene	−23.4 ± 0.4
toluene	−27.8 ± 0.3
n-perfluorohexane	−31.5 ± 0.4
n-perfluorooctane	−40.7 ± 0.3
perfluoromethylcyclohexane	−31.9 ± 0.2
perfluorobenzene	−38.7 ± 0.2
perfluorotoluene	−32.3 ± 0.3
2,3,4,5,6-pentafluorotoluene	−36.0 ± 0.2
4-fluorotoluene	−30.1 ± 0.2

Table 5. Activity Coefficients at Infinite Dilution at 45 °C

solute	$\ln(a_1/w_1)^\infty$ at 45 °C
n-heptane	4.7 ± 0.2
n-octane	4.8 ± 0.2
n-nonane	5.1 ± 0.2
n-decane	5.3 ± 0.2
methylcyclohexane	4.3 ± 0.2
benzene	4.4 ± 0.2
toluene	4.5 ± 0.2
n-perfluorohexane	1.4 ± 0.3
n-perfluorooctane	1.1 ± 0.2
perfluoromethylcyclohexane	1.2 ± 0.2
perfluorobenzene	1.9 ± 0.2
perfluorotoluene	1.3 ± 0.2
2,3,4,5,6-pentafluorotoluene	2.5 ± 0.2
4-fluorotoluene	4.1 ± 0.2

negative values of ΔH_s. Bearing in mind eq 8, this can be related to both the variations of enthalpies ΔH_c and ΔH_m. To get the answer to this question, let us consider the variation of the partial molar enthalpy of mixing ΔH_m of hydrocarbons and fluorocarbons with poly(TFE/PMVE).

The most rigorous way for finding the ΔH_m values is a consideration of the temperature dependence of the activity coefficients according to eq 7b. The weight fraction activity coefficients can serve as a measure of free energy of mixing (eq 7a). The larger are the values of $(a_1/w_1)^\infty$, the less thermodynamically favorable is the process of mixing. The values of the activity coefficients for different solutes are compared at 45 °C in Table 5. Unusually high values of $(a_1/w_1)^\infty$ are observed for hydrocarbons in poly(TFE/PMVE). For example, the $(a_1/w_1)^\infty$ values in the range 110−220 are observed for *n*-alkanes C_7−C_{10}. For comparison, the $(a_1/w_1)^\infty$ values of hydrocarbon solutes in common, hydrogen-based polymers are lower by at least 1 order of magnitude.[41−44]

Besides using the temperature dependence of $(a_1/w_1)^\infty$, a common, though approximate, way for finding the ΔH_m values is an application of eq 8 (see e.g. refs 10 and 36). Here, one neglects nonideality of the vapor phase. In such calculations, the enthalpy of condensation can be taken at standard temperatures, e.g., at corresponding boiling point,[26] or after taking into account its temperature dependence according to Reid and Sherwood.[25] Both ways were employed in this work, and the results are compared in Table 6.[45] It can be seen that, for all the solutes, different approaches for calculation give qualitatively similar trends for hydrocarbons and fluorocarbons, though in many cases the differences are beyond the statistical error indicated in the second column of the table. The mixing process is strongly endothermic for hydrocarbons. For fluorocarbons, the ΔH_m values become exothermic; however, the absolute values of ΔH_m are not large, as compared, for example, to the mixing process in some high free volume glassy polymers.[12,36,46]

Table 6. Partial Molar Enthalpy of Mixing ΔH_m into Poly(TFE−PMVE)[a]

solute	ΔH_m,[b] kJ/mol	ΔH_m,[c] kJ/mol	ΔH_m,[d] kJ/mol
n-heptane	12.5 ± 1.1	9	13
n-octane	8.3 ± 0.3	4	10
n-nonane	9.5 ± 0.2	4	13
n-decane	11.8 ± 0.2	4	14
methylcyclohexane	8.8 ± 0.5	6	9
benzene	8.9 ± 0.4	7	9
toluene	7.9 ± 0.3	3	7
n-perfluorohexane	−1.8 ± 0.4	−6	−5
n-perfluorooctane	−3.8 ± 0.1	*e*	*e*
perfluoromethylcyclohexane	−0.7 ± 0.2	0	−1
perfluorobenzene	0.7 ± 0.5	−1	2
perfluorotoluene	−7.5 ± 0.2	−9	−5
2,3,4,5,6-pentafluorotoluene	2.5 ± 0.2	0	6
4-fluorotoluene	6.9 ± 0.2	5	9

[a] The sources of the data for ΔH_c are refs 25, 27, and 31. [b] Based on temperature dependence of the activity coefficients in the range 45−100 °C. [c] Based on the formula $\Delta H_m = \Delta H_s - \Delta H_c$ using ΔH_c enthalpies of condensation at the boiling points. [d] Based on the formula $\Delta H_m = \Delta H_s - \Delta H_c$ using temperature dependent ΔH_c as calculated according to Reid and Sherwood.[25] [e] The value of the enthalpy of condensation for this compound seems to be at odds with the reported values for other fluorocarbons.

Regarding the values of the enthalpies of sorption, ΔH_s, one can conclude that the more negative values observed for fluorocarbons are caused mainly by exothermic enthalpies of mixing. Because of the low cohesion energy density of fluorocarbons, their enthalpies of condensation are less exothermic than corresponding values for hydrocarbons.

Detailed studies of sorption thermodynamics in glassy polymers using the IGC method revealed[46,36] that the partial molar enthalpies of mixing ΔH_m vary in a wide range of values and strong effects of solute size (e.g., its critical volume) on this parameter are observed. On the other hand, the ΔH_m values in hydrocarbon-based rubbery polymers are confined to a rather narrow range of values for the same solutes. Table 6 shows that the range of variation of the ΔH_m values in poly(TFE/PMVE) is more or less the same as in previously investigated hydrocarbon-based rubbers (see e.g. ref 47). However, the process of mixing of the perfluorinated rubber with hydrocarbons is characterized by more endothermic (positive) values of ΔH_m, while exothermic mixing is observed for fluorocarbons. No distinct effects of solute's size on the ΔH_m values can be seen in the case of rubbery poly(TFE/PMVE). This is consistent with the concept that such effects in glassy polymers are related to filling of free volume elements in a polymer.

4.3. Flory−Huggins Parameter. The dissolution of vapors in a rubbery polymer is usually described using the Flory−Huggins model[48]

$$\ln a_1 = \ln \varphi_2 + (1 - \varphi_2) + \chi_{12}(1 - \varphi_2)^2 \qquad (13)$$

where $a_1 = p/p_s$ is solute activity in the vapor phase, φ_2 is the volume fraction of sorbed molecules, and χ_{12} is the Flory−Huggins interaction parameter. The Flory−Huggins equation is widely employed to model sorption in rubbery polymers due, in part, to its ease of use and because it allows characterizing the entire, usually observed exponential sorption isotherm by means of a single parameter. Sometimes, a free volume component is partitioned in the χ_{12} value,[49] but its contribution is minor in rubbers as compared with the term describing the contact interactions in formation of the polymer−solute mixture. IGC enables a direct determination of the Flory−Huggins parameter using eq 9. The resulting temperature dependence of χ_{12} for various solutes is shown in Figure 5. As expected for

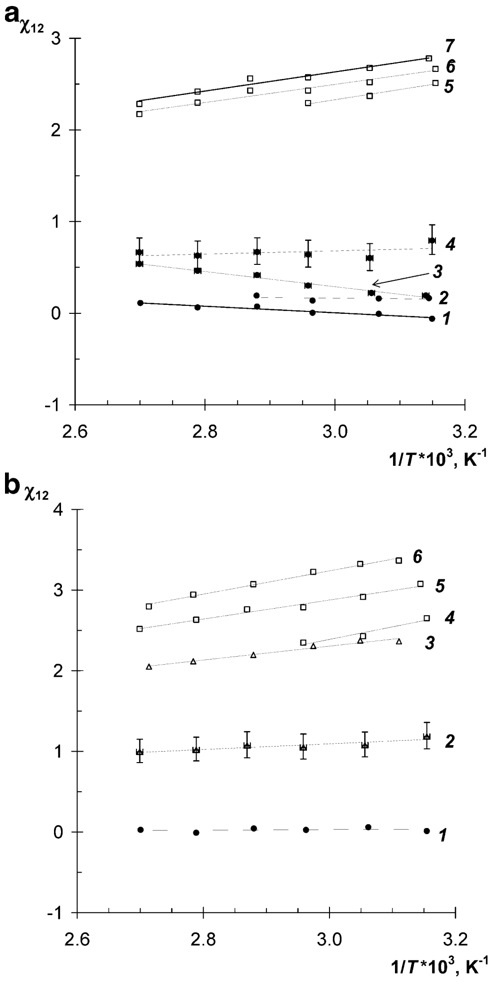


Figure 5. Temperature dependence of the Flory−Huggins χ_{12} parameter: (a) 1, *n*-perfluorooctane; 2, *n*-perfluorohexane; 3, perfluorotoluene; 4, perfluorobenzene; 5, benzene; 6, toluene; 7, *n*-octane; (b) 1, perfluoromethylcyclohexane; 2, 1,2,3,4,5-pentafluorotoluene; 3, 4-fluorotoluene; 4, *n*-heptane; 5, *n*-nonane; 6, *n*-decane. The data for methylcyclohexane overlap those of 4-fluorotoluene and benzene, so for clarity the former is not shown in this figure.

hydrocarbons, which are nonsolvents for poly(TFE/PMVE), very large positive χ_{12} values are observed. They can be compared with the χ_{12} values found for the systems hydrocarbon−low molecular mass poly(perfluoroalkyl ether), $[(OCFCF_3CF_2)_n-(OCF_2)_m]$.[50] For various aliphatic and cycloaliphatic hydrocarbons they were in the range 2.4−3.3. In both cases, Flory−Huggins parameters of this magnitude reflect unfavorable thermodynamic interaction of C−H bonds with perfluorinated medium. The χ_{12} values observed for perfluorinated solutes are mainly in the range 0−0.5, or even negative, indicating good affinity of the polymer to these compounds. For partly fluorinated toluene derivatives, intermediate χ_{12} values are observed. An increase in temperature results in a decrease in χ_{12} for hydrocarbons and an increase for fluorocarbons, thus reflecting positive and negative values of ΔH_m, respectively (cf. eqs 6 and 9).

In the investigation of gas sorption in poly(TFE/PMVE) by the static volumetric method,[19] the authors suggested correlating solubility coefficients by the linear equation

$$\ln S = -(4.5 + \chi_0) + (6/T - \chi_1)T_c \qquad (14)$$

where the adjustable parameters χ_0 and χ_1 are defined by the formula

$$\chi_{12} = \chi_0 + \chi_1 T_c \qquad (15)$$

The results of the study of the same polymer using IGC can be used to check this assumption. An examination of Figure 5 indicates that the Flory−Huggins parameters at constant temperature indeed increase when the size of a solute increases (e.g., from *n*-heptane to *n*-decane). In a more quantitative manner, the correlations $\chi_{12}-T_c$ were treated separately for aliphatic hydrocarbons and fluorocarbons. The following equations (at 45 °C) were found for hydrocarbons

$$\chi_{12} = 0.0097T_c - 2.61 \qquad (16)$$

and for fluorocarbons

$$\chi_{12} = -0.0044T_c + 2.17 \qquad (17)$$

By substituting these into eq 14, the following correlations were found in the approximation of the linear correlation of ln *S* and T_c, namely for hydrocarbons

$$\ln S = 0.010T_c - 1.9 \qquad (18)$$

and for fluorocarbons

$$\ln S = 0.024T_c - 6.7 \qquad (19)$$

Therefore, the slope is significantly higher for fluorocarbons, in agreement with the observation made by Prabhakar et al.[19] at slightly lower temperature.

Experiments with partially fluorinated toluene molecules ($C_6H_5CH_3$, $C_6H_4FCH_3$, $C_6F_5CH_3$, $C_6F_5CF_3$) enabled an examination of the effects of hydrogen replacement by fluorine within the structure of the same carbon skeleton. A linear decrease in the Flory−Huggins parameter, as seen in Figure 6, as well as in $\ln(a_1/w_1)^\infty$ (and hence free energy of mixing ΔG_m) is observed when the number of introduced fluorine atoms increases. Similarly, values of ΔH_m and ΔS_m decrease nonlinearly. This indicates that mainly contact interactions between C−H and C−F bonds of solutes and C−F bonds of the polymer are responsible for the observed thermodynamic parameters. It is worthwhile to note that this result is in line with the observed solubility of lower hydrocarbons/fluorocarbons in low molecular mass hydrocarbon and fluorocarbon solvents.

4.4. Solubility Parameter. As has been mentioned, the IGC method enables a determination of the solubility parameter of polymers.[28] Using eq 10, one can find the solubility parameter δ_2 of the polymer via the slope and the intercept of this linear dependence.

The definition of the solubility parameter is based on regular solution theory.[51] It is known that the core idea of this approach is the fulfillment of geometric mean rule for the interaction energy of two components (*i* and *j*) in solutions:

$$\epsilon_{ij} = (\epsilon_{ii}/\epsilon_{jj})^{1/2} \qquad (20)$$

This theory is often not valid for solutions of low molecular mass hydrocarbons (HC) and fluorocarbons (FC), while it holds for binary solutions of hydrocarbons and fluorocarbons.[52−54] Similar effects have been noted for HC/FC systems where one of the components is a polymer, that is, for solutions of FC in a hydrocarbon-based polymer (poly(dimethylsiloxane)) and solutions of HC in perfluorinated polymer.[55,56] Nevertheless, it is interesting to explore this problem once more for a big group of fluorocarbons and hydrocarbons in perfluorinated rubber poly(TFE−PMVE) using IGC as a tool.

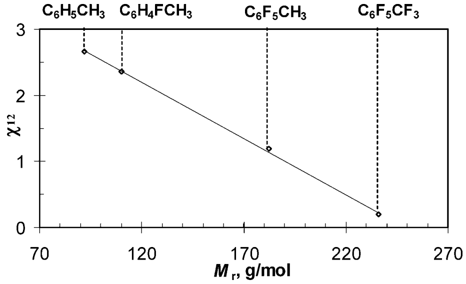


Figure 6. Flory−Huggins χ_{12} parameters in partly fluorinated toluene derivatives.

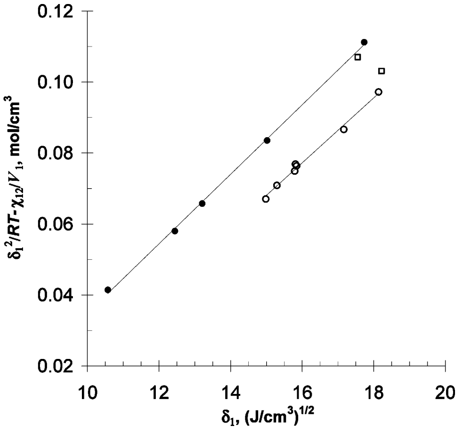


Figure 7. Estimation of solubility parameter δ_2 in poly(TFE−PMVE) at 45 °C: filled circles, fluorocarbons; open circles, hydrocarbons; squares, partly fluorinated hydrocarbons.

Figure 7 presents an example of the dependence described by eq 10 at 45 °C for poly(TFE−PMVE). The values of δ_1 at different temperatures were computed using the well-known Hildebrand formula[51]

$$\delta_1 = \left(\frac{\Delta H_v - RT}{V_1}\right)^{1/2} \tag{21}$$

where ΔH_v (J/mol) is the enthalpy of vaporization and V_1 (cm^3/mol) is mole volume of the solute. These parameters were calculated as recommended by Reid and Sherwood.[25] As shown, perfluorinated and hydrocarbon solutes form two independent lines. This method for the determination of δ_2 has been applied to polystyrene and poly(methyl acrylate) (above their T_g)[28] and for glassy poly(vinyltrimethylsilane).[57] In these studies, mainly hydrocarbons served as solutes. For all the systems investigated, single dependences in the coordinates defined by eq 10 were obtained, and the δ_2 values estimated via the slopes and intercepts were in excellent agreement. So for the first perfluorinated polymer studied using the IGC method we observe two separate dependences for fluorocarbon and hydrocarbon solutes. This behavior is similar to separate correlations observed for solubility coefficients of HC and FC in perfluorinated polymers according to several works[10,12] and shown in Figure 4 for poly(TFE−PMVE). One can assume that in both cases the same reasons related to nature of intermolecular interactions in these systems are responsible for appearance of differing dependences for HC and FC.

The values of the solubility parameters δ_2 obtained are presented in Table 7. The agreement between δ_2(slope) and δ_2(intercept) is excellent for the line obtained by sorption of fluorocarbons. On the other hand, the agreement is much worse for the values obtained in experiments with hydrocarbons as the solutes. We speculate that the δ_2 values obtained from the experiments with fluorocarbons are more reliable because regular solution theory is less successful for description of the system poly(TFE−PMVE)−hydrocarbons.

Table 7. Solubility Parameter δ_2 (J/cm^3)$^{1/2}$ of Poly(TFE−PMVE) at 45 °C

line for perfluorinated solutes		line for hydrocarbon solutes	
slope	intercept	slope	intercept
12.9 ± 0.2	12.9 ± 0.2	12.1 ± 0.5	13.5 ± 0.5

It is tempting to compare the value of δ_2 for poly(TFE−PMVE) obtained here with those reported for other perfluorinated polymers. Such a comparison is not simple for several reasons. First, the value found via IGC refers to the infinite dilution conditions, while common methods for determination of the solubility parameters are based on measurements with finite solute concentration (viscosity, swelling, and surface tension methods). Since many perfluorinated polymers are semicrystalline and nonsoluble, the data are not abundant. Standard references report values of 12−13 (J/cm^3)$^{1/2}$ and 12.7 (J/cm^3)$^{1/2}$ for poly(tetrafluoroethylene).[58,59] Both values are rather close to that found in the present work. These values are among the smallest for all the polymers studied and reflect reduced interchain and surface energy of perfluorinated polymers.

5. Conclusions

The following conclusions can be made as a result of the chromatographic study of sorption of numerous hydrocarbons, fluorocarbons, and partly fluorinated hydrocarbons in amorphous, rubbery poly(TFE−PMVE).

1. Solubility coefficients of aliphatic, cycloaliphatic, and aromatic fluorocarbons in this perfluorinated rubber are markedly higher than those of their hydrocarbon analogues. These differences are larger for heavier solutes. Solubility coefficients of all the vapors studied increase proportionally to the square of the critical temperature, T_c^2, but hydrocarbons and fluorocarbons exhibit separate dependences. The data for lower alkanes and fluoroalkanes reported earlier are consistent with the results of chromatographic study of higher hydrocarbons and fluorocarbons, so unified correlations of ln S vs T_c^2 are observed in a wide range of variation of T_c, that is, between 190 and 620 K.

2. The temperature dependencies of the solubility coefficients indicated that the enthalpies of sorption ΔH_s of fluorocarbons in poly(TFE−PMVE) are noticeably more negative than those of hydrocarbons. The estimated values of partial molar enthalpy of mixing ΔH_m of fluorocarbons with poly(TFE−PMVE) are slightly negative, which is unusual for rubbery materials. It can reflect affinity between fluorocarbons and perfluorinated polymer. On the other hand, strongly endothermic ΔH_m values are observed for hydrocarbons, thus mirroring repulsive forces between these solutes and perfluorinated polymer chains.

3. The Flory−Huggins interaction parameters χ_{12} in poly(TFE−PMVE) were found for different solutes at various temperatures. Hydrocarbons are characterized by large and positive values of χ_{12}, reflecting unfavorable thermodynamic interactions of C−H bonds and the perfluorinated medium. For fluorocarbons they are in the range 0−0.5 or even negative. This is indicative of good affinity of the polymer with these compounds. For partly fluorinated hydrocarbons Flory−Huggins parameters χ_{12} have intermediate values: a good linear correlation is observed between χ_{12} and the number of fluorine atoms introduced into the toluene molecule.

4. Using IGC data, the solubility parameter of poly(TFE−PMVE) $\delta_2 = 12.9 \pm 0.2$ $(J/cm^3)^{1/2}$ was found on the basis of sorption data for perfluorinated solutes. Excellent agreement between the δ_2 values found via the slope and the intercept of the corresponding dependence is evidence of the reliability of the obtained value as well as a comparison with the δ_2 values of other perfluorinated polymers. On the other hand, less reliable results were obtained on the basis of sorption data of hydrocarbons. These results seem to be a consequence of a limited applicability of the regular solution theory to the system “perfluorinated polymer−hydrocarbons”.

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