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## Thermodynamics of Sorption in an Amorphous Perfluorinated Copolymer AF1600 Studied by Inverse Gas Chromatography

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**ABSTRACT:** Detailed investigation of infinite dilution sorption of organic vapors ( $C_7$ – $C_{16}$  *n*-alkanes, toluene, octafluorotoluene, *p*-fluorotoluene, 2,3,4,5,6-pentafluorotoluene, perfluorooctane) in perfluorinated copolymer AF1600 (random copolymer of 35 mol % perfluoroethylene and 65 mol % 2,2-bis-(trifluoromethyl)-4,5-difluoro-1,3-dioxole) was performed by inverse gas chromatography (IGC).  $C_{13}$ – $C_{16}$  *n*-alkanes were studied in the temperature range including both glassy and rubbery states of the polymer, while sorption of other solutes was investigated only in the glassy state of the perfluorinated copolymer. Retention diagrams of  $C_{13}$ – $C_{16}$  *n*-alkanes showed breakpoints at  $\sim 150$  °C which corresponds to  $T_g$  of AF1600. Thermodynamic analysis of IGC data in rubbery and glassy states was performed based on the model developed earlier which included evaluation of Flory–Huggins interaction parameter  $\chi$  and glassy state structural parameters: excess free volume  $\phi_v^0$ , polymer cohesion energy  $\epsilon_{22}$ , and entropy depression term  $s_{12}$ . It was shown that aliphatic and aromatic hydrocarbons were poor solvents for glassy AF1600. Positive  $\chi$  values substantially increased when the length of the alkane increases. Fluorinated hydrocarbons were, however, good solvents for AF1600, and their quality improved with the increase in fluorination degree. On the basis of the cohesion energy of AF1600 ( $-17.76$  kJ/mol) evaluated by CAChe 7.5 molecular modeling package, excess free volume of AF1600 in the glassy state was found to be close to 0.12 and slightly dependent on temperature. The entropy effect of sorption in glassy polymer was highly negative with entropy depression proportional to molar volume of solute.

### 1. Introduction

Sorption of vapors in polymers is important from fundamental and applied points of view (membrane separation, polymer processing, etc.). In most cases, polymer “sorbents” have been studied either below or above the glass transition temperature  $T_g$ , i.e., in the glassy or rubbery state. It is interesting to observe changes of sorption thermodynamic parameters in passing through  $T_g$  of the polymer, though such studies are not numerous. Drastic changes of solubility coefficients and enthalpies of sorption of light gases have been observed earlier for rubbery and glassy states of poly(*N*-isopropylacrylamide) (poly(NIPAM)),<sup>1</sup> poly-(vinyltrimethylsilane) (PVTMS), and metathesis poly(trimethylsilylnorbornene) (PTMSN).<sup>2</sup> Interesting objects of the studies of such kind can be polymers with higher fractional free volume (FFV) having  $T_g$  values suitable for investigation below and above  $T_g$ . An amorphous random copolymer of 65 mol % 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and 35 mol % tetrafluoroethylene (AF1600), a well-known commercial product, can be a convenient object for such study with suitable FFV (0.27–0.32) and  $T_g$  ( $\sim 160$  °C).<sup>3,4</sup>

There are a number of methods for investigation of solubility in polymers.<sup>5</sup> Among them, inverse gas chromatography (IGC) possesses several advantages: instrumental simplicity, possibility of rapid testing in a wide temperature range for a large set of solutes (vapors). In addition, the method allows investigating the polymers in a state which is not perturbed by a large amount of absorbed vapor, namely, at infinite dilution region. For polymers

with sufficiently large diffusivity like AF1600, one may study the bulk sorption of volatile probes of widely varying molecular mass (e.g., *n*-alkanes and fluorine-containing substances) in both the rubbery and glassy states.

So the aim of the present work was to investigate vapor sorption thermodynamics in possibly wider range of temperature including  $T_g$  and for wide range of solutes of different size and nature by IGC.

Sorption of gases and vapors in the glassy AF1600 has been studied by Alentiev et al.<sup>3</sup> and De Angelis et al.<sup>6</sup> In the first work, the classical dual mode sorption model was applied, and its parameters were obtained based on sorption isotherms of a number of gases.<sup>3</sup> Langmuir sorption capacities  $C_H'$  of gas–AF1600 systems confirmed high fraction of free volume in the polymer. De Angelis et al.<sup>6</sup> compared experimental isotherms of gases in glassy AF1600 with those predicted or correlated by the nonequilibrium lattice fluid (NELF) model. Characteristic parameters of the pure AF1600 were determined by fitting to the Sanchez–Lacombe equation of state<sup>7</sup> experimental *PVT* data above  $T_g$ . First-order approximation of NELF (adjustable parameter  $\Psi = 1$ ) was sufficient to correlate sorption isotherms of  $N_2$  and  $O_2$  while heavier solutes (light hydrocarbons and fluorocarbons) demanded second-order approximation ( $\Psi < 1$ ).

In principle, several approaches have been developed to describe thermodynamics of sorption behavior of solutes in glassy polymers. The Vrentas and Vrentas model<sup>8</sup> uses a direct relation between excess sorption capacity and excess free energy of glassy polymer in comparison with rubbery one. The excess free energy is determined by difference between specific heat capacities of rubbery-like and glassy polymers. A number of

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quantities should have been introduced in order to account for concentration devitrification and thermal expansion of the sorption system.

Leibler and Sekimoto<sup>9</sup> showed that the distinctive features of sorption in glassy systems may be related to their elastic properties, namely, bulk modulus  $K_{gl}^0$  of glassy polymer. They demonstrated a simple relationship between the change of the specific heat capacity  $\Delta c_p$  at the glass transition and the elastic modulus  $K_{gl}^0$  of a glass in attempt to relate both (their<sup>9</sup> and Vrentas–Vrentas<sup>8</sup>) models. Hence, determination of transition concentration  $\phi_g(T)$  of polymer becomes a weak point of the theory.

Another approach attempting to explain thermodynamic behavior of (glassy polymer)–solute systems was developed earlier by one of the authors<sup>10,11</sup> of this work. It was based on Flory–Huggins thermodynamic theory modified to account for nonequilibrium structure of glassy polymers which was characterized by several parameters with clear physical meaning: volume fraction of metastable voids (excess free volume of the glass), polymer cohesion energy, and entropy depression from allocation of solute molecule in metastable void. Hence, another aim of the present work was testing this theory by IGC data obtained for AF1600.

It is worth noting once more that the thermodynamic parameters were obtained in the conditions of infinite dilution. Their extension to higher activities, i.e., for the conditions that can be met in the processes of membrane separation, requires a special consideration. In this work the conditions of the infinite dilution were used for characterization of pure, undisturbed polymer. It can be assumed taking into account the results of refs 10 and 11 that using this model the IGC results can be extended to wider range of compositions.

## 2. Background

In the IGC studies, the retention times of sorbed  $t_r$  and “non-sorbed” component  $t_a$  are measured.<sup>12</sup> Actually, the value  $t_a$  corresponds to the almost nonsorbed component (usually air) and is necessary to allow for the dead volume of the chromatograph. Thus, the net retention volume  $V_N$  can be found:

$$V_N = (t_r - t_a)F_{\bar{p}_x, T} \quad (1)$$

where  $F_{\bar{p}_x, T}$  is the volumetric flow rate of the carrier gas at a pressure averaged over the length of the chromatographic column and temperature  $T$ . The values of  $F_{\bar{p}_x, T}$  are determined in the following way:

$$F_{\bar{p}_x, T} = F_{p_0, T_a} j_3^2 \frac{T}{T_a} \quad (2)$$

where  $F_{p_0, T_a}$  is the volumetric flow rate of the carrier gas measured at atmospheric pressure  $p_0$  and room temperature  $T_a$ ;  $j_3^2$  is the James–Martin correction factor, which is equal to the ratio of the pressure  $\bar{p}_x$  averaged over the length of the chromatographic column and the pressure  $p_0$  at the outlet of the column.<sup>13</sup>

After accounting for the mass  $w_L$  (g) of the polymer in the column, the specific retention volume  $V_g$  can be calculated:

$$V_g = \frac{V_N}{w_L} \quad (3)$$

$V_g$  is the main experimental value which can be used for the evaluation of all thermodynamic parameters.

The IGC method can be applied to determine the solubility coefficient at infinite dilution provided quite a small amount of the solute is injected into the column:<sup>14</sup>

$$S = \frac{1}{p_0^2} \rho_2 V_g \exp\left(-\frac{2B_{13} - V_1}{RT} p_0 j_4^3\right) \quad (4)$$

Here,  $p^0 = 1$  atm is the standard value,  $\rho_2$  is the density of the polymer, and the mixed virial coefficient  $B_{13}$  and the molar volume  $V_1$  of the solute allow for the solute nonideality. These values are used in accordance with recommendations.<sup>15</sup> The value  $p_0$  is the pressure at the inlet of the column, and the parameter  $j_4^3$  is a correction equal to the ratio between the pressure averaged over the sample retention time in the chromatographic column and the pressure at the outlet of the column.<sup>13</sup>

The starting point of IGC application in thermodynamics of polymer solutions is the relation between experimental value of net retention volume and partition coefficient  $k_p$  of solute between stationary liquid (polymeric) and moving gas phases:<sup>16</sup>

$$k_p = \frac{C_{1,L}}{C_{1,G}} = \frac{V_N}{V_L} \quad (5)$$

where  $C_{1,L}$  and  $C_{1,G}$  are molar concentrations of solute in liquid and gas phases and  $V_L$  is the volume of stationary phase. According to the basic thermodynamic consideration,<sup>17</sup> equilibrium partition of volatile component between gas and liquid phases at low external pressure is given by

$$\frac{x_{1,G}}{x_{1,L}} = \gamma_1 \frac{P^0}{P} \quad (6)$$

where  $x_{1,G}$  and  $x_{1,L}$  are molar fractions of solute in gas and liquid phases,  $P^0$  is saturated pressure of solute at given temperature,  $P$  is external pressure, and  $\gamma_1$  is the activity coefficient of solute in liquid phase formally defined as  $a_1/x_{1,L}$  ( $a_1$  being the activity of solute in liquid phase).

Combined with eq 5 and ideal gas law, eq 6 can be transformed into general relation between specific retention volume and activity coefficient of the solute in polymer phase at infinite dilution:<sup>16</sup>

$$\ln \gamma_1^\infty = \lim_{x_1 \rightarrow 0} (\ln a_1 - \ln x_{1,L}) = \ln \frac{RT}{V_g P_1^0 M_2} \quad (7)$$

where  $M_2$  is the molar mass of liquid phase, which is polymer molar mass in particular.

According to the classical Flory–Huggins theory of polymer solutions, the activity of the solute in polymer solution is given by<sup>18</sup>

$$\ln a_1 = \frac{\Delta\mu_1}{RT} = \ln \varphi_1 + \left(1 - \frac{1}{r}\right) \varphi_2 + \chi \varphi_2^2 \quad (8)$$

where  $\varphi_1$  and  $\varphi_2$  are volume fractions of solute and polymer in stationary phase,  $\Delta\mu_1$  is the chemical potential of dissolution for the solute,  $r$  is the polymerization degree, and  $\chi$  is the binary interaction parameter (Flory–Huggins parameter).

Introduction of eq 8 into eq 7 gives the following:

$$\ln \frac{RT}{V_g P_1^0 M_2} = \lim_{\varphi_2 \rightarrow 1} \left[ \ln \frac{\varphi_1}{x_{1,L}} + \left(1 - \frac{1}{r}\right) \varphi_2 + \chi \varphi_2^2 \right]$$

Taking into account that in terms of Flory–Huggins lattice model

$$\frac{\varphi_1}{x_1} = \frac{1}{r}$$

and

$$M_2 = r M_{\text{segm}}$$

where  $M_{\text{segm}}$  is molar mass of polymer segment (monomer unit), we finally obtain very compact relation between the binary

interaction parameter  $\chi$  at infinite dilution and the specific retention volume of the solute.

$$\ln \frac{RT}{V_g P_1^0 M_{\text{segm}}} = \left(1 - \frac{1}{r}\right) + \chi^\infty \quad (9)$$

In classical Flory–Huggins theory it is assumed that solute molecules and monomer units occupy equal cells in the lattice, which means that they should necessarily have equal molar volumes. However, usually solute molecules differ substantially in their size from monomer units in polymer chain. In order to resolve this contradiction, segment of the polymer should be assigned to be the same size as solute molecule. It means that the cells of the effective lattice in the solution have got the size of solute molecule and will necessarily contain several monomer units of the polymer. Of course, if the monomer unit of the polymer is larger than the solute molecule, the effective cell should be taken to fit monomer units first. In typical IGC studies solute molecules are larger than the monomer units and based on it  $M_{\text{segm}}$  in eq 9 should be substituted with  $M_1$ , molar weight of the solute, and actual polymerization degree  $r$  with the number of effective segments  $r^*$ .

On the basis of these considerations, and introducing a correction term for nonideality of gas phase into eq 9, finally we obtain the following equation for binary interaction parameter of the solute–polymer pair:

$$\chi^\infty = \ln \frac{RT}{V_g P_1^0 M_1} - \frac{P_1^0}{RT} (B_{11} - V_1) - \left(1 - \frac{1}{r}\right) \quad (10)$$

Equation 10 is exactly the same as obtained by Patterson et al.<sup>16</sup> It is worth mentioning here that eq 10 was originally obtained in ref 16 based on rather disputable empirical assumption that activity coefficient  $\gamma_1$  in polymer stationary phase might be substituted by  $a_1/\omega_1$  ( $\omega_1$  being the weight fraction of the solute instead of its molar fraction). The analysis given above indicates that empirical assumption of Patterson<sup>16</sup> is not at all inevitable, and the same result can be obtained in a rigorous way.

Like any other thermodynamic equation based on the Flory–Huggins theory, eq 10 is applicable to the elastic flexible polymers with relatively weak interactions. In the case of more complex systems eq 10 should rather be generalized:

$$\frac{\Delta\mu_{1,\text{noncomb}}^\infty}{RT} = \ln \frac{RT}{V_g P_1^0 M_1} - \frac{P_1^0}{RT} (B_{11} - V_1) - \left(1 - \frac{1}{r}\right) \quad (11)$$

The left-hand side of eq 11,  $\Delta\mu_{1,\text{noncomb}}^\infty$ , accumulates all non-combinatorial contributions to the chemical potential of the solute at infinite dilution. In particular, if adsorption occurs on the surface of a glassy polymer, it includes contribution from non-equilibrium glassy structure of the stationary phase. As AF1600 exists in glassy state at ambient temperature, this case is of special interest within the framework of the present study.

According to the model proposed earlier,<sup>10,11</sup> noncombinatorial chemical potential of the solvent is the sum of two contributions:

$$\Delta\mu_{1,\text{noncomb}} = \Delta\mu_{1,\text{res}} + \Delta\mu_{1,\text{gl}} \quad (12)$$

where the residual term  $\Delta\mu_{1,\text{res}}$  accounts for molecular interaction in the solution and  $\Delta\mu_{1,\text{gl}}$  for the nonequilibrium nature of the glassy state of the polymer and its relaxation during sorption of the solute. In polymer solutions with relatively weak interactions residual term is usually taken as the sum of enthalpy ( $\chi_H$ ) and entropy ( $\chi_S$ ) binary interaction parameters. The glassy structure contains nonequilibrium voids which form excess free volume of the glassy polymer. During penetration of the solute into polymer these voids get filled with solute molecules. It must result in large

and negative contributions both to the enthalpy and to the entropy of mixing. According to this theoretical approach non-combinatorial chemical potential of the solute at infinite dilution can be expressed as follows:<sup>10</sup>

$$\frac{\Delta\mu_{1,\text{noncomb}}^\infty}{RT} = \chi^\infty + \frac{\varepsilon_{22} - Ts_{12}}{RT} \phi_V^0 (z - 1) \quad (13)$$

where  $\varepsilon_{22}$  is the cohesion energy of the polymer,  $s_{12}$  the entropy depression parameter,  $\phi_V^0$  the volume fraction of nonequilibrium voids in the initial polymer structure, and  $z$  the coordination number of the effective lattice. In liquid solutions the latter parameter is usually set to 8–10. On the other hand, as proposed in refs 10 and 11, it can be taken as  $(1 - \phi_V^0)/\phi_V^0$ , which corresponds to the volume fraction of polymer segments around nonequilibrium voids. Then eq 13 becomes

$$\frac{\Delta\mu_{1,\text{noncomb}}^\infty}{RT} = \chi^\infty + \frac{\varepsilon_{22} - Ts_{12}}{RT} (1 - 2\phi_V^0) \quad (14)$$

From this equation excess enthalpy  $\bar{h}_1^{E,\infty}$  and entropy  $\bar{s}_1^{E,\infty}$  of the solute at infinite dilution can be derived according to basic thermodynamic equations:

$$\bar{h}_1^{E,\infty} = \frac{\partial(\Delta\mu_{1,\text{noncomb}}^\infty/T)}{\partial(1/T)} = RT\chi_H^\infty + \varepsilon_{22} (1 - 2\phi_V^0) \quad (15)$$

$$\bar{s}_1^{E,\infty} = -\frac{\partial\Delta\mu_{1,\text{noncomb}}^\infty}{\partial T} = -R\chi_S^\infty + s_{12}(1 - 2\phi_V^0) \quad (16)$$

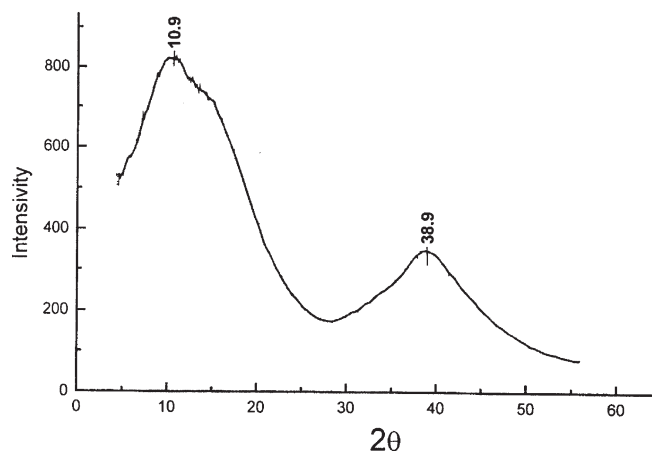
### 3. Experimental Section

**3.1. Materials.** Teflon AF1600 was purchased from DuPont (Wilmington, DE) and used as received. According to the supplier, its molecular mass is 100 000, the glass transition temperature is 156–162 °C, and the density is 1.8 g/cm<sup>3</sup>.<sup>4,19</sup> Wide-angle X-ray data (Figure 1) indicate that AF1600 is a fully amorphous material. The diffractogram includes two wide peaks (amorphous halos) with  $2\theta$  angles at 10.9° and 38.9°. The same behavior is characteristic for other high free volume polymers (polytrimethylsilylpropyne, addition-type poly(trimethylsilylnorbornene), etc.).<sup>20</sup>

A set of accurately selected solutes was used in this study. They included *n*-alkanes C<sub>7</sub>–C<sub>16</sub>, toluene, octafluorotoluene, perfluorooctane, and toluene derivatives containing both H and F atoms: 4-fluorotoluene and 2,3,4,5,6-pentafluorotoluene. All the solutes studied had purity not less than 98%. A single peak retention time was measured in the chromatographic experiments.

**3.2. Chromatographic Procedure.** Macroporous solid carrier Inerton AW, with surface area about 0.5 m<sup>2</sup>/g, and a particle size of 0.16–0.20 mm was coated by the perfluorinated copolymer AF1600. The deposition of AF1600 was performed from a 1 wt % solution in perfluorotoluene. 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 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 3.5 ± 0.1 wt %. The measurements in the range 65–190 °C were performed using a CrystaLux 4000 chromatograph with thermal conductivity detector and a stainless steel column with the length 2 m and inner diameter 2 mm. The vapor dose was introduced with a syringe, using a dose size of about 1 μmol. The temperature of the sample evaporator was kept at 30 °C higher than the boiling point of the solute. Helium served as a gas carrier, and air peak was used for estimation of  $t_a$ . Retention time was determined on the maximum value of the





**Figure 1.** X-ray plots for glassy AF1600.

chromatographic peak. In order to introduce the corrections into eqs 2 and 4, the inlet pressure was checked using a high sensitivity manometer ( $\pm 0.01$  kPa), while the outlet pressure was taken as atmospheric. Seven parallel measurements were carried out for each solute at each temperature.

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 (or net) retention volume as a function of gas flow rate  $F_{p_x,T}$ .<sup>21</sup> The flow rate in the experiments must be less than a certain limiting value such that there will be no dependence of  $V_N$  (or  $V_g$ ) on  $F_{p_x,T}$ . Examples at 110 and 140 °C are shown in Figure 2. Slight slopes are observed in all the cases, and the higher is the *n*-alkane, the larger is the slope. But, fortunately, the intercepts do not differ from the values at lowest flow rate if one takes into consideration their discrepancies (Figure 2). Thus, the equilibrium regime of dynamic sorption is reached at flow rate 5 cm<sup>3</sup>/min, so this flow rate was used in the experiments at these and higher temperatures. Retention times  $t_r$  did not depend on the size of injected sample having the order of 1  $\mu$ mol. It means that the thermodynamic parameters determined corresponded to the infinite dilution conditions.<sup>21</sup>

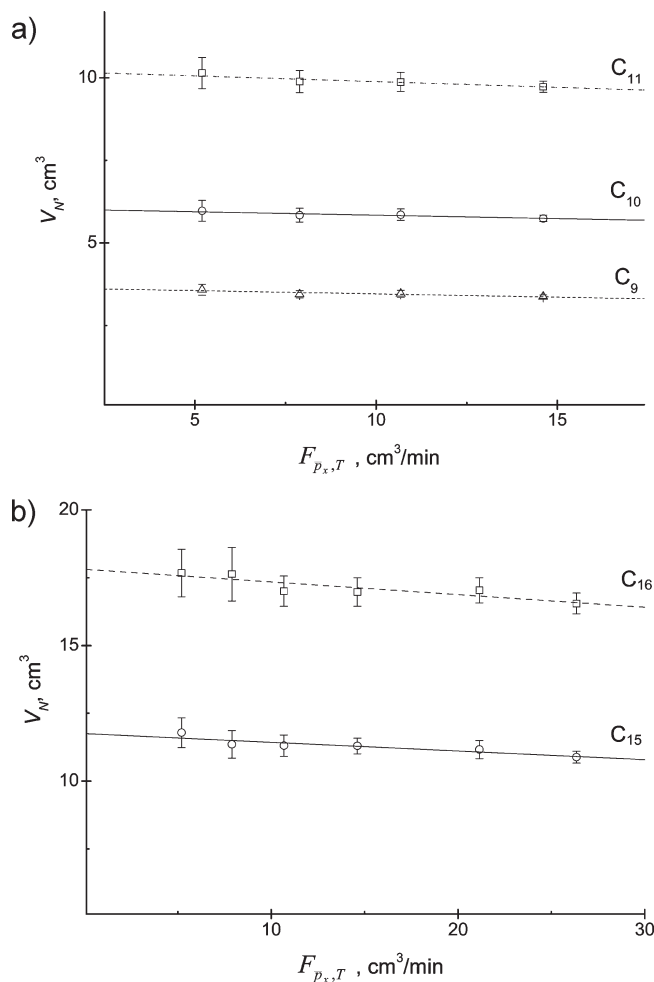
Saturated vapor pressures of the solutes were found according to the Antoine equation and/or the equation  $\ln P_{VP} = A \ln T + B/T + C + DT^2$ , as calculated using the Korean<sup>22</sup> or NIST<sup>23</sup> databases. Temperature dependencies of density of liquid C<sub>13</sub>–C<sub>16</sub> *n*-alkanes were retrieved from the available literature.<sup>24–27</sup>

The temperature dependence of the polymer density (or specific volume) at atmospheric pressure has been reported by Dlubek et al.<sup>4</sup> based on the experimental values obtained by Dr. J. Pionteck and kindly provided to us. The original experimental data were approximated by the linear function  $\rho_2(T) = AT + B$ , where  $T$  is the temperature (K) and  $\rho_2(T)$  is expressed in g/cm<sup>3</sup>: for glassy state  $A = (-6.45 \pm 0.03) \times 10^{-4}$  g/(cm<sup>3</sup> K),  $B = 2.040 \pm 0.001$  g/cm<sup>3</sup>; for rubbery state  $A = (-19.5 \pm 0.3) \times 10^{-4}$  g/(cm<sup>3</sup> K),  $B = 2.61 \pm 0.02$  g/cm<sup>3</sup>.

## 4. Results and Discussion

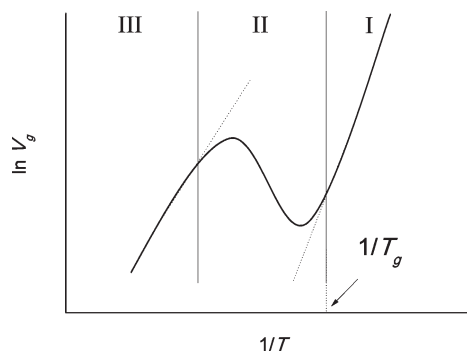
### 4.1. Retention Diagrams and Intrinsic Energies of Sorption.

Retention diagrams, the dependences of  $\ln V_g$  vs reciprocal temperature, are commonly discussed plots if determination of  $T_g$  of a polymer is carried out by the IGC investigation.<sup>12,21,28</sup> For amorphous polymers three regions on the retention diagram (Figure 3) below and above  $T_g$  were distinguished by Guillet and Braun.<sup>29</sup> At higher temperature in region III a solute is sorbed into the bulk and surface of a rubbery polymer. In the region II, solute diffusion coefficient (in conventional polymers) turns out to be insufficient for establishing sorption equilibrium in the whole film of the polymer; hence, the diffusion limitations appear. Therefore,



**Figure 2.** Effect of the gas carrier flow rate  $F_{p_x,T}$  on the net retention volumes  $V_N$  of *n*-alkanes in the glassy AF1600: (a) C<sub>9</sub>–C<sub>11</sub> at 110 °C; (b) C<sub>15</sub>, C<sub>16</sub> at 140 °C.

sorption capacity of the polymer is reduced with decreasing temperature until the equilibrium bulk sorption becomes zero, and therefore, the total retention volume will be comprised only by adsorption on the polymer surface. Such behavior has been earlier demonstrated for PS,<sup>29</sup> PMMA,<sup>30</sup> PVC,<sup>31</sup> etc. In region I (glassy state) when one moves from lower to higher temperature the retention of a solute decreases as temperature increases up to glass transition temperature of the polymer. This picture does not hold for highly permeable polymers with large free volume<sup>32</sup> and in particular AF1600.<sup>3</sup> Even below  $T_g$  of this polymer the solutes under investigation are sorbed into the bulk. First, it is manifested in the linearity of retention diagrams of the solutes below  $T_g$  as is seen in Figure 4a,b. Indeed, the correlation coefficients obtained for these lines are close to 1:  $R^2 = 0.986$  for *n*-perfluorooctane and  $R^2 \geq 0.997$  for the other solutes (*n*-alkanes and substituted toluenes). Second, there are no diffusion limitations for bulk sorption in glassy polymer and hence no region II on retention diagrams of C<sub>13</sub>–C<sub>16</sub> *n*-alkanes as is demonstrated in Figure 4c. It seems to be a rather rare IGC observation of such kind of behavior among polymers studied. According to author's knowledge, similar dependencies were obtained by Guillet et al.<sup>1</sup> for poly(*N*-isopropylacrylamide), Arnould et al.<sup>33</sup> for poly(methyl methacrylate) and poly(*p*-methylstyrene) via the IGC method, and Kamiya et al.<sup>2,34</sup> using equilibrium gravimetric gas sorption experiments for PVTMS, PTMSN, polycarbonate,



**Figure 3.** Scheme of Z-shaped retention diagram of solute below and above  $T_g$ .<sup>29</sup>

and poly(methyl methacrylate). It can be added that linear retention diagrams can be observed also for conventional glassy polymers if they are present in the chromatographic column in extremely thin films.<sup>12</sup> The reason for the absence of the breaks in Figure 4a,b is lower temperature range used in the study of these solutes: even highest  $T$  is lower than  $T_g$ .

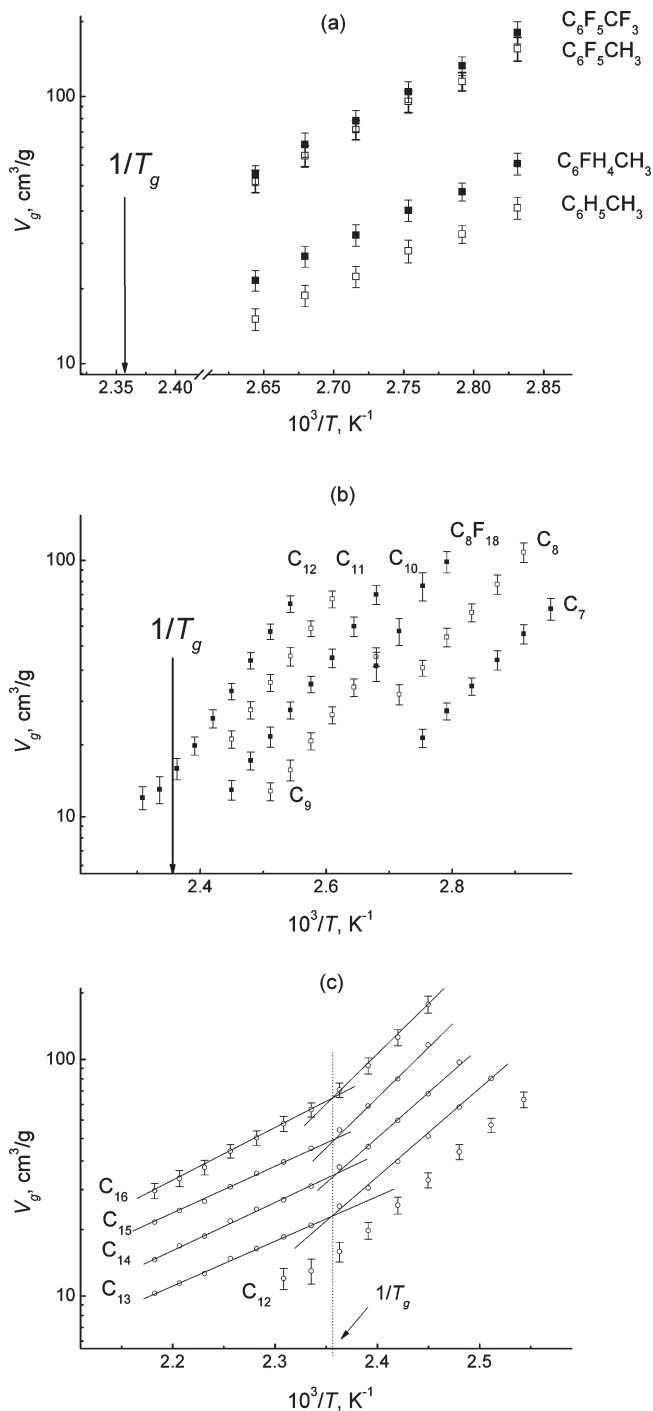
The temperature of the breakpoints ( $\sim 150^\circ\text{C}$ ) at the retention diagrams of solutes from  $C_{13}$  to  $C_{16}$  (Figure 4c) is very close to  $T_g$  of this polymer reported by the producer and obtained by DSC and PVT data.<sup>4,19</sup> Thus, we may certainly attribute the breakpoints at retention diagrams to glass transition in AF1600.

The presence of two straight lines with different slopes with the breaks at  $T_g$  indicates two different mechanisms (and the range of variation of the observed thermodynamic parameters) of absorption below and above  $T_g$ . In the glassy state, high exothermic intrinsic energies  $U_1^S$  were observed. The negative values of  $U_1^S$  are much larger by absolute value than intrinsic energies of condensation (Table 1). For  $n$ -alkanes, the values  $U_1^S$  observed in the glassy state of AF1600 increase as the size of hydrocarbon increases. In rubbery state,  $U_1^S$  values are much lower than those in glassy state (for  $C_{13}$ – $C_{16}$   $n$ -alkanes) and slightly lower than energies of condensation. It reflects unfavorable interactions in the systems with rubbery AF1600 and the  $n$ -alkanes assuming a condensation of the vapor in the rubbery matrix of the polymer. For the set of fluorinated derivatives of toluene, a higher number of F atoms in the molecule of fluorine-containing toluenes results in more exothermic sorption (this will be discussed in detail below).

The changes of the enthalpy of sorption  $\Delta H_S$  of gases and vapors when passing from the glassy to the rubbery state have been discussed in the literature. Thus, Kamiya et al.<sup>2,34,35</sup> observed breaks in the van't Hoff plots for the solubility coefficients measured by gravimetric methods in several polymers. Similar breaks were observed for the solubility coefficients estimated as the ratio  $P/D$ , where  $P$  is the permeability coefficient and  $D$  is the diffusion coefficient.<sup>36</sup> In most cases the values of  $\Delta H_S$  at  $T > T_g$  are less negative than  $\Delta H_S$  at  $T < T_g$ . This can be explained by the well-known relationship

$$\Delta H_S = \Delta H_c + \Delta H_m \quad (17)$$

where  $\Delta H_c$  is the enthalpy of condensation and  $\Delta H_m$  is the partial molar enthalpy of mixing. The latter value is strongly negative for glassy polymers,<sup>37</sup> while in the rubbery state it is close to zero or slightly positive (endothermic).<sup>12</sup> The value of  $\Delta H_c < 0$  is the characteristics of vapor–liquid equilibrium of a solute and is independent of nature and physical state of a polymer studied.<sup>38</sup> Hence, the sum (17) should be more negative below  $T_g$ , in accordance with the data obtained.



**Figure 4.** Retention diagrams of solutes under investigation in the perfluorinated copolymer AF1600.

**4.2. Solubility Coefficient.** IGC experimental results allow also an estimation of the solubility coefficients  $S$  at infinite dilution. For a set of solutes with wide range of critical temperatures ( $T_c$ ) they are often presented as a correlation of  $\log S$  vs  $T_c^2$  or  $(T_c/T)^2$ .<sup>39,40</sup> The solubility coefficients of  $n$ -alkanes  $C_7$ – $C_{16}$  for AF1600 (reduced to  $35^\circ\text{C}$ <sup>48</sup>) determined in the present work are in agreement with the data of lighter hydrocarbons reported earlier<sup>41</sup> (Figure 5a). The correlation for the systems AF1600– $n$ -alkanes is located between the corresponding correlations for other glassy perfluorinated polymers (AF2400,<sup>41</sup> Hyflon AD80<sup>42</sup>); however, its ability to dissolve  $n$ -alkanes is much greater than that of rubbery

**Table 1. Intrinsic Energies of Sorption of Solutes in Perfluorinated Copolymer AF1600**

solute	$U_1^S$ , kJ/mol		$U_1^{\text{cond}}$ at $T_b$ , kJ/mol
	glassy	rubbery	
<i>n</i> -heptane	-47.3 ± 0.6		28.7
<i>n</i> -octane	-53 ± 1		31.1
<i>n</i> -nonane	-61 ± 1		34.3
<i>n</i> -decane	-62.5 ± 0.6		35.0
<i>n</i> -undecane	-65.0 ± 0.5		37.6
<i>n</i> -dodecane	-69.2 ± 0.6		39.6
<i>n</i> -tridecane	-73.6 ± 0.3	-37.7 ± 1	41.4
<i>n</i> -tetradecane	-76 ± 1	-39.3 ± 1	43.2
<i>n</i> -pentadecane	-84 ± 5	-40 ± 1	44.9
<i>n</i> -hexadecane	-84 ± 3	-44 ± 1	46.6
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	-42 ± 1		30.6
C <sub>6</sub> FH <sub>4</sub> CH <sub>3</sub>	-44 ± 1		31.5
C <sub>6</sub> F <sub>5</sub> CH <sub>3</sub>	-50 ± 1		32.2
C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub>	-54 ± 1		26.6
<i>n</i> -perfluorooctane	-71 ± 6		30.8

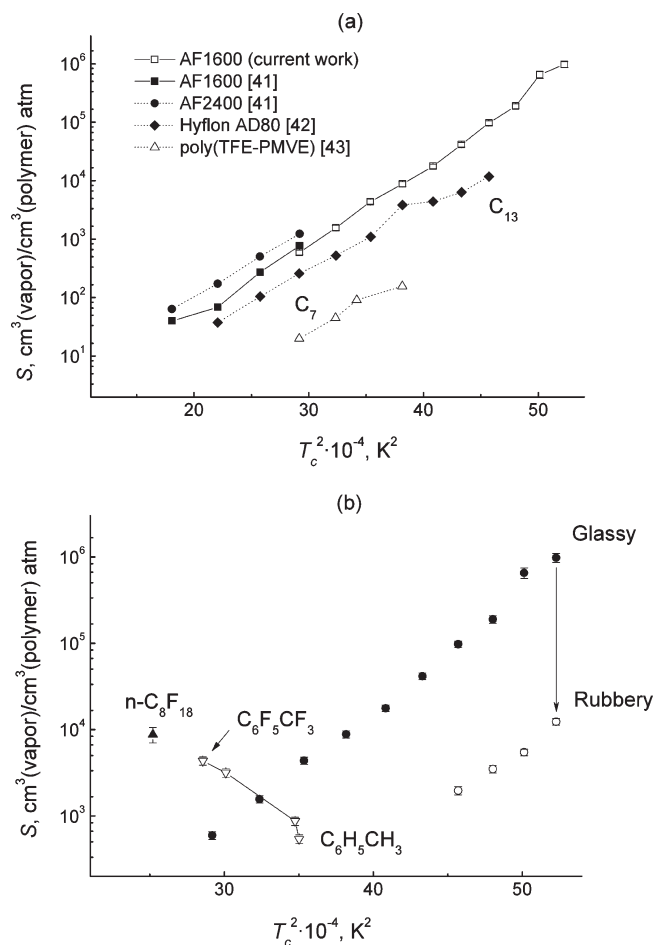
copolymer of tetrafluoroethylene and perfluoromethyl vinyl ether, poly(TFE-PMVE)<sup>42</sup> (Figure 5a).

It is possible to extrapolate the part of the retention diagrams above  $T_g$  to 35 °C and estimate apparent solubility coefficients of C<sub>13</sub>–C<sub>16</sub> *n*-alkanes in AF1600 as if they were “rubbery” at this temperature. The results of such extrapolation are shown in Figure 5b. It is seen that the values obtained in this way are much lower than actual solubility coefficients of the same solutes in glassy AF1600.

It is worth noting that solubility coefficients of *n*-alkanes regularly increase as condensability of the solute increases in both glassy and rubbery polymers (Figure 5a). However, we face opposite behavior for fluorine-containing derivatives of toluene. The solubility coefficient  $S$  of this series decrease as the critical temperature becomes higher (Figure 5b). A main cause of this decreasing may be apparently a gradual reduction of affinity between the perfluorinated matrix and the solutes as the number of fluorine atoms increases in the molecule of the solute, which has been recently demonstrated for the same set of solutes in rubbery poly(TFE-PMVE).<sup>43</sup> A similar tendency of decreasing  $S$  is observed for *n*-perfluorooctane and *n*-octane (Figure 5b) in spite of higher condensability of the latter. These results for the first time explicitly indicate that condensability of vapor is not the only factor that affect the affinity between polymer and solute: local interactions (attraction or repulsion) can also strongly contribute the observed solubility coefficients.

**4.3. Evaluation of Thermodynamic Parameters of Interaction between AF1600 and Solutes.** Let us first consider enthalpy of interaction between AF1600 and solutes which is represented by excess enthalpy  $\bar{h}_1^{E,\infty}$  of solute at infinite dilution. Equation 15 for experimental values of  $\bar{h}_1^{E,\infty}$  contains three adjustable molecular parameters:  $\varepsilon_{22}$ ,  $\phi_V^0$  which correspond to polymer phase and  $\chi_H$  which is the characteristic of polymer–solute interactions. Only one parameter can be calculated by means of eq 15 using experimental data, while others should be evaluated separately.

The cohesion energy of polymer  $\varepsilon_{22}$  has clear physical meaning and can be successfully estimated by various incremental approaches.<sup>44</sup> In the present study for this purpose we used computational program CAChe 7.5 by Fujitsu,<sup>45</sup> which provides an opportunity for calculating polymer cohesion energy based on molecular model of monomer unit. The calculation gave  $\varepsilon_{22} = -7.67$  kJ/mol for PTFE and  $-23.20$  kJ/mol for poly(perfluorodioxole). As AF1600 is the copolymer of 65% perfluorodioxole and 35% of tetrafluoroethylene  $\varepsilon_{22}$  for AF1600 was calculated as the proportional sum of two values given above, which resulted in  $-17.76$  kJ/mol. This

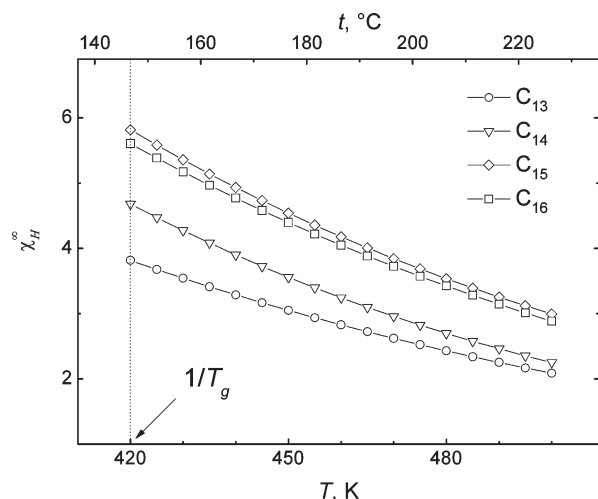


**Figure 5.** Correlation of solubility coefficients with square of critical temperature of solute: (a) comparison of solubility coefficients of *n*-alkanes in AF1600 with other perfluorinated polymers; (b) comparison of solubility coefficients of solutes in AF1600.

value is higher than that for PTFE but substantially lower than for PS ( $-36.93$  kJ/mol) or PVC ( $-52.30$  kJ/mol), indicating that perfluorinated polymers, as is well-known, are characterized by much lower cohesion energy than typical commercial polymers. The value  $-17.76$  kJ/mol for  $\varepsilon_{22}$  of AF1600 will be used below throughout all calculations.

A specific feature of AF1600 is its relatively high permeability, which stems from low density of packing of macromolecular chains.<sup>3,4</sup> From this point of view the volume fraction  $\phi_V^0$  of nonequilibrium voids in AF1600 structure is of major importance. In order to calculate its value from eq 15, we have analyzed dependencies  $\ln V_g(1/T)$  for C<sub>13</sub>–C<sub>16</sub> alkanes both above and below  $T_g$ .

In the temperature range above  $T_g$  AF1600 is in its equilibrium rubbery state, and its structure contains no nonequilibrium voids ( $\phi_V^0 = 0$ ). Thus, the glassy state contribution to  $\bar{h}_1^{E,\infty}$  vanishes, and according to eq 15,  $\bar{h}_1^{E,\infty} = RT\chi_H$ . The values of  $\bar{h}_1^{E,\infty}$  were calculated by differentiation of eq 11 vs the reciprocal temperature. Therefore, we used the slope of linear dependence of  $\ln V_g(1/T)$  above  $T_g$  (Figure 4c) and analytical derivative of  $P_1^0$  which was calculated using the Korean DataBase.<sup>22</sup> Figure 6 presents calculated temperature dependence of enthalpy interaction parameter  $\chi_H$  for C<sub>13</sub>–C<sub>16</sub> alkanes at temperatures above  $T_g$  of AF1600 (the values are normalized to the effective molar volume of AF1600 monomer unit). One can see that  $\chi_H$  values are positive and decrease when temperature increases. It means that interaction between the solutes and the polymer become



**Figure 6.** Temperature dependence of  $\chi_H^\infty$  for C<sub>13</sub>–C<sub>16</sub> *n*-alkanes above  $T_g$  of AF1600.

**Table 2.** Parameters of Equation  $\chi_H^\infty = a + bT + cT^2$  for C<sub>13</sub>–C<sub>16</sub> Solutes

solute	<i>a</i>	<i>b</i> × 10, K <sup>−1</sup>	<i>c</i> × 10 <sup>4</sup> , K <sup>−2</sup>	<i>R</i> <sup>2</sup>
C <sub>13</sub>	29.0	−0.92	0.77	0.99
C <sub>14</sub>	56.5	−2.01	1.86	0.99
C <sub>15</sub>	60.9	−2.12	1.92	0.99
C <sub>16</sub>	54.6	−1.86	1.65	0.99

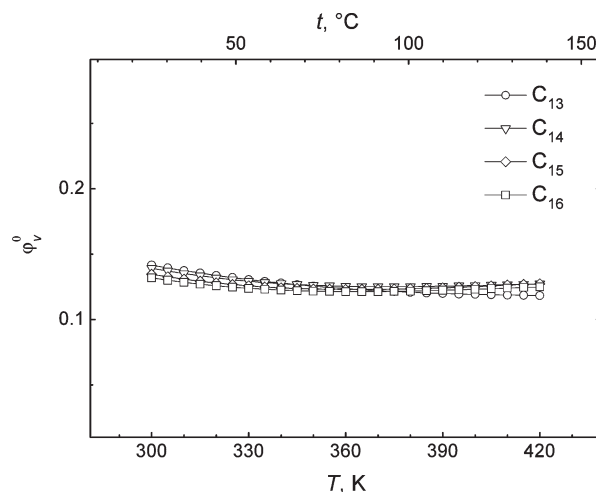
more favorable. The curves are fitted very well with parabolic trends, whose numerical parameters are given in Table 2.

It can be assumed that the parabolic trends of  $\chi_H^\infty$  smoothly proceed below  $T_g$  of AF1600 so this dependence can be used to evaluate binary interaction parameter for C<sub>13</sub>–C<sub>16</sub> alkanes in the glassy state of AF1600. We believe it to be a reasonable approximation, since vitrification is not a first-order phase transition and the nature of molecular interactions should not change significantly. Since  $\chi_H^\infty$  and  $\epsilon_{22}$  have been determined, it is possible to evaluate nonequilibrium voids fraction  $\phi_V^0$  in AF1600 glassy structure by means of eq 15. Therefore, we differentiate eq 11 in the same manner as described above using the slope of linear dependence of  $\ln V_g(1/T)$  below  $T_g$ .

As has been noted, the slope of  $\ln V_g(1/T)$  drastically changes at  $T_g$  (Figure 4c), which results in an increase in absolute values of  $h_1^{E,\infty}$  for the glassy AF1600. According to approach developed in refs 10 and 11, the reason for this is a large exothermal effect of penetration of solute molecules into nonequilibrium voids that appear in polymer structure below  $T_g$ . The physical origin of this effect can be qualitatively explained as follows.

When solute molecule penetrates into equilibrium liquid structure, a certain energy is needed to overcome molecular cohesion forces inside liquid to provide some space for the solute molecule. It implies endothermic contribution to the total enthalpy of mixing. Meanwhile, in nonequilibrium glassy structure such space preexists due to lacking in mobility of macromolecular chains below  $T_g$ . Therefore, there is no need to overcome cohesion forces during penetration of solute molecule into nonequilibrium voids in glassy polymer structure and endothermic contribution vanishes. It results in total enthalpy gain. In a nutshell, high negative enthalpy of dissolution in glassy structure is not the result of stronger molecular interactions but is rather owing to less cohesion contacts to overcome.

The temperature dependence of  $\phi_V^0$  values calculated for C<sub>13</sub>–C<sub>16</sub> solutes is given in Figure 7. One can see that despite



**Figure 7.** Temperature dependence of nonequilibrium voids fraction in AF1600 glassy structure calculated for C<sub>13</sub>–C<sub>16</sub> solutes.

the differences in  $\ln V_g$  and  $\chi_H^\infty$  values for individual C<sub>13</sub>–C<sub>16</sub> solutes (see Figures 4c and 6), calculated values of  $\phi_V^0$  are very close. We believe it to be certain justification of the approach applied, since due to physical reasons  $\phi_V^0$  should be the characteristic feature of a polymer but not solutes. The mean value for the entire temperature range for C<sub>13</sub>–C<sub>16</sub> solutes is 12.6%, which seems to be quite reasonable. On the basis of Figure 7, it can be assumed that  $\phi_V^0$  trend below  $T_g$  will be also valid for sorption of any solute within glassy AF1600 structure.

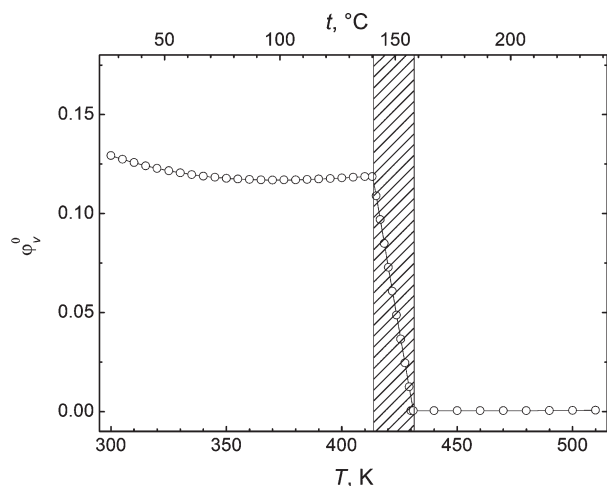
Figure 8 presents the averaged  $\phi_V^0$  trend above and below  $T_g$  of AF1600. In order to calculate  $\phi_V^0$  in the vicinity of  $T_g$ , the actual derivatives of parabolic interpolation for  $\ln V_g(1/T)$  plots near the breakpoint were used.

One can see from Figure 8 that  $\phi_V^0$  remains zero above  $T_g$  and very rapidly increases up to almost constant level  $\phi_V^0 \approx 0.12$  around  $T_g$  with some trend for an increase upon further cooling. The region of drastic increase of  $\phi_V^0$  corresponds to the transition region around  $T_g$  in Figure 4c, where the slope of retention volume plots changes between adjacent linear interpolations.

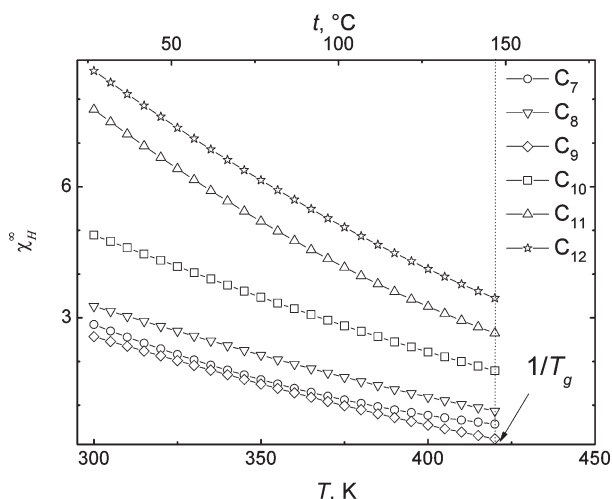
The stepwise manner of  $\phi_V^0$  change was not expected, as a priori we would rather presume more or less gradual increase of  $\phi_V^0$  values below  $T_g$  in accordance with the results of temperature dependencies of the specific volume below and above  $T_g$  reported in refs 4 and 6. However, the obtained steps stemmed directly from the linearity of retention volume plots below  $T_g$ . Apparently, it means that  $\phi_V^0$  is the effective model thermodynamic parameter, more sensitive to the changes in molecular interactions rather than to the actual volume changes of the polymer. Some additional discussion of  $\phi_V^0$  trend will be given below concerning entropy changes.

The  $\phi_V^0$  values can be compared with FFV found for this polymer using different approaches. According to Dlubek et al.<sup>4</sup> and Prabhakar et al.,<sup>46</sup> the FFV values are in the range 0.186–0.30. It means that  $\phi_V^0$  corresponds only to a part of total free volume in glassy polymer. A plausible explanation for it can be as follows. As is seen from Figure 8 in the rubbery state  $\phi_V^0$  (nonequilibrium fraction of free volume according to refs 10 and 11) is equal to zero. It does not mean that the rubbery phase does not include free volume: the amorphous polymer in equilibrium state above  $T_g$  contains microcavities of fluctuation nature. After transition to the glassy state these microcavities are frozen, and the corresponding FFV can include the  $\phi_V^0$  estimated in the present work.





**Figure 8.** Temperature dependence of nonequilibrium voids fraction in AF1600 glassy structure.

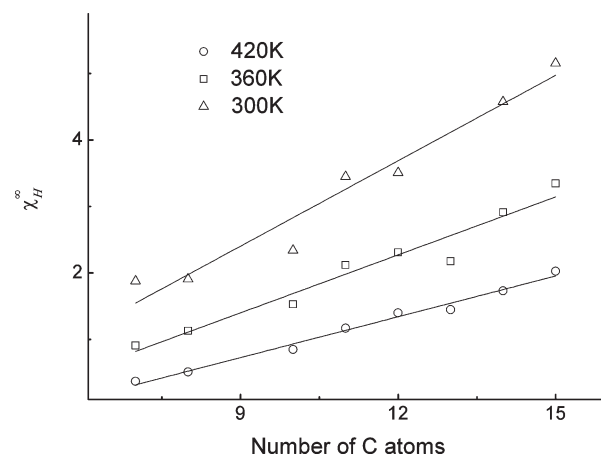


**Figure 9.** Temperature dependence of  $\chi_H^\infty$  for C<sub>7</sub>–C<sub>12</sub> *n*-alkanes below  $T_g$  of AF1600.

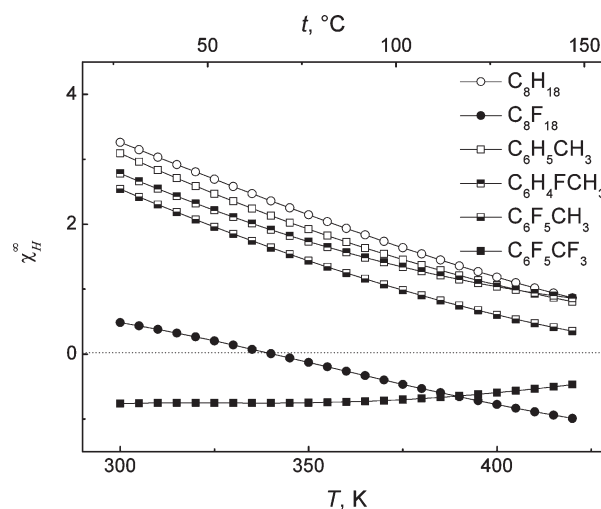
The characteristic  $\phi_v^0(T)$  dependence for AF1600 was used to calculate binary interaction parameter  $\chi_H^\infty$  for all other solutes by means of eq 15. Figure 9 presents  $\chi_H^\infty(T)$  plots for C<sub>7</sub>–C<sub>12</sub> alkanes. One can see the same trend of the improvement of binary interaction between polymer and solute with temperature.

Figure 10 shows the influence of the length of alkane's chains on  $\chi_H^\infty$ , the parameter that characterizes the interaction between solutes and AF1600 in the vicinity of  $T_g$  and below it. One can see that with the increase in the length of alkane molecule its interaction with AF1600 weakens almost linearly.

It is interesting to compare binary interaction parameter of alkanes with that for fluorinated solutes which can be calculated in the same manner. One can see that fluorination of solutes substantially improves their binary interaction with AF1600. While C<sub>8</sub>H<sub>18</sub> is a poor solvent over the entire temperature range ( $\chi_H^\infty > 0.5$ ) below  $T_g$ , perfluorinated octane C<sub>8</sub>F<sub>18</sub> is a good one ( $\chi_H^\infty < 0.5$ ), and furthermore  $\chi_H^\infty$  for the latter solute is negative above 340 K, which accounts for good solubility of AF1600 in perfluoroalkanes. The same trend of the improvement of interaction exists among aromatic solutes. Consequent introduction of fluorine atoms in toluene results in a decrease in binary interaction parameter (Figure 11).



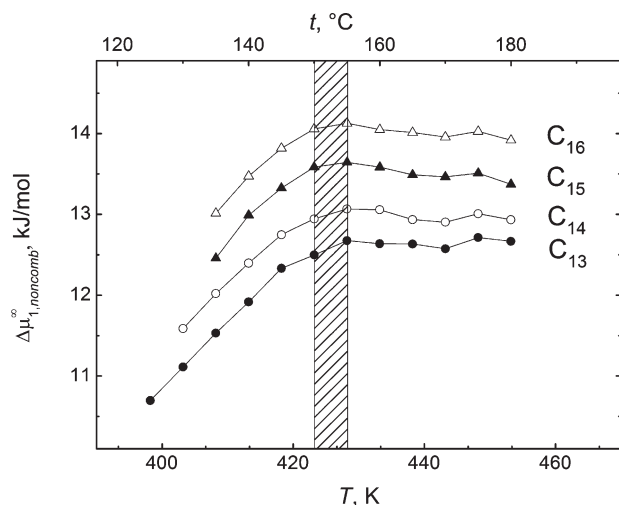
**Figure 10.** Influence of the length of *n*-alkane molecule on  $\chi_H^\infty$ .



**Figure 11.** Temperature dependence of  $\chi_H^\infty$  for fluorinated solutes below  $T_g$  of AF1600.

**4.4. Evaluation of Entropy Parameters of Sorption in AF1600.** Infinite dilution excess entropies of solutes were calculated by eq 16. Temperature dependencies of infinite dilution noncombinatorial chemical potential of C<sub>13</sub>–C<sub>16</sub> solutes in temperature ranges of elastic and glassy states of AF1600 are presented in Figure 12. The breakpoints can be clearly seen in the vicinity of glass transition temperature of AF1600. The slope of the temperature dependence is infinite dilution excess partial entropy of solute with reversed sign ( $-\bar{s}_1^{E,\infty}$ ). The values of  $\bar{s}_1^{E,\infty}$  (Table 3) are negative for C<sub>13</sub>–C<sub>16</sub> below  $T_g$  and positive above it (except for C<sub>13</sub> in which case  $\bar{s}_1^{E,\infty}$  is negative but very close to zero). According to general thermodynamic relations negative sign of entropy corresponds to ordering processes while positive sign does to disordering, which then are dominant trends in sorption of alkanes in AF1600 below and above its  $T_g$  in respect. The absolute values of  $\bar{s}_1^{E,\infty}$  in the glassy state are at least by 1 order of magnitude higher than that in the rubbery state (Table 3). Thus, ordering trend definitely prevails upon disordering below glass transition temperature.

According to eq 16, there are two contributions to  $\bar{s}_1^{E,\infty}$ . The first one corresponds to noncombinatorial entropy of interaction between AF1600 and the solute and is represented by  $\chi_S^\infty$ . It accounts for the changes in thermodynamic probability due to the interaction between the polymer and the solvent. The second contribution to  $\bar{s}_1^{E,\infty}$  stems from



**Figure 12.** Temperature dependencies of infinite dilution noncombinatorial chemical potential of C<sub>13</sub>–C<sub>16</sub> *n*-alkanes.

**Table 3.** Entropy Parameters of Sorption of C<sub>7</sub>–C<sub>16</sub> *n*-Alkanes in AF1600

solute	$\bar{s}_1^{E,\infty}$ rubbery, J/(mol K)	$\chi_S^\infty$		$\bar{s}_1^{E,\infty}$ glassy, J/(mol K)	$s_{12}$ , J/(mol K)
		per mole of solutes	per mole of AF1600 units		
C <sub>7</sub>				–50.6	–66.5
C <sub>8</sub>				–64.8	–85.1
C <sub>9</sub>				–79.0	–104
C <sub>10</sub>				–75.3	–99
C <sub>11</sub>				–73.4	–97
C <sub>12</sub>				–78.8	–103
C <sub>13</sub>	–0.795	0.095	0.036	–81.5	–107
C <sub>14</sub>	0.55	–0.067	–0.024	–77.3	–102
C <sub>15</sub>	7.90	–0.951	–0.317	–86.6	–114
C <sub>16</sub>	5.62	–0.676	–0.208	–80.4	–106

nonequilibrium glassy nature of the polymer. According to the theory used, it depends on the volume fraction of nonequilibrium voids  $\phi_V^0$  which was evaluated above in section 4.3 and entropy depression parameter  $s_{12}$ .

As it is shown in Figure 9,  $\phi_V^0$  vanishes above  $T_g$ , and  $\chi_S^\infty$  is the only contribution to  $\bar{s}_1^{E,\infty}$  in this temperature range. Values of  $\chi_S^\infty$  normalized to the effective molar volume of AF1600 monomer unit (Table 3) are close to zero or slightly negative, which indicates that some disordering takes place during sorption of alkanes in AF1600 at  $T > T_g$ . However, the absolute values of  $\chi_S^\infty$  do not exceed 0.32, which is by at least 1 order of magnitude lower than  $\chi_H^\infty$  values for the same solutes given above (Table 2 and Figure 6). It means that enthalpy contribution to Flory–Huggins parameter substantially dominates over entropy.

At  $T < T_g$  eq 16 includes both contributions to  $\bar{s}_1^{E,\infty}$ . One may suppose that noncombinatorial entropy of binary interaction does not drastically change at  $T_g$  for the same reason as enthalpy of interaction, namely because vitrification is not first-order phase transition. However,  $\bar{s}_1^{E,\infty}$  values do drastically change at  $T_g$  (Table 3). So one may assume that the reason for such changes is contribution of nonequilibrium glassy structure of AF1600. As one can see from Table 3, the absolute values of  $\bar{s}_1^{E,\infty}$  in the rubbery state are almost within the accuracy of calculation of  $\bar{s}_1^{E,\infty}$  in the glassy state. We think it to be the evidence that glassy state contribution substantially dominates over noncombinatorial entropy of interaction between solutes and AF1600. A similar conclusion was given above concerning comparison between  $\chi_H^\infty$  and  $\chi_S^\infty$ .

**Table 4.** Entropy Parameters of Sorption of Fluorine-Containing Hydrocarbons, *n*-Octane, and Toluene in AF1600

solute	$\bar{s}_1^{E,\infty}$ glassy, J/(mol K)	$s_{12}$ , J/(mol K)
<i>n</i> -C <sub>8</sub> F <sub>18</sub>	–95.8	–125.7
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	–64.82	–85.1
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	–44.13	–57.9
C <sub>6</sub> H <sub>4</sub> FCH <sub>3</sub>	–44.20	–58.0
C <sub>6</sub> F <sub>5</sub> CH <sub>3</sub>	–49.37	–65.3
C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub>	–62.3	–81.8

Taking all this into account, we assumed that in the first approximation noncombinatorial entropy of interaction might be neglected, and we used  $\chi_S^\infty \approx 0$  in further analysis for all solutes.

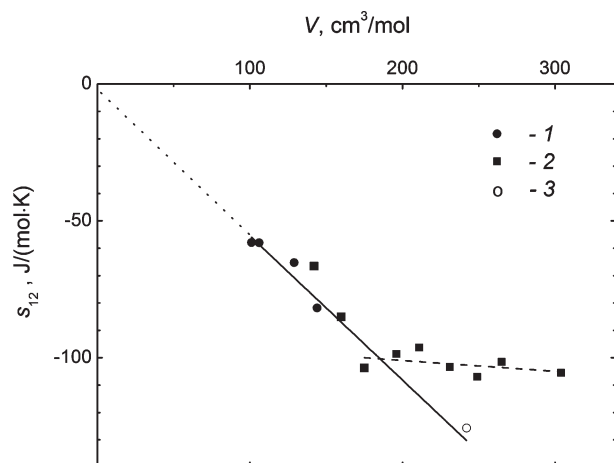
Without noncombinatorial term  $-R\chi_S^\infty$  eq 16 reduces to glassy state contribution in  $\bar{s}_1^{E,\infty}$  which equals  $s_{12}(1 - 2\phi_V^0)$ . Then it allows one calculating the values of  $s_{12}$  parameter that characterizes depression of entropy at sorption in metastable voids of glassy structure of AF1600 below  $T_g$ . In the calculations we put on that  $\phi_V^0 = 0.12$  (see section 4.3),  $s_{12}$  values for *n*-alkanes are listed in Table 3 and for fluorinated hydrocarbons in Table 4.

The parameter  $s_{12}$  is strongly negative for all solutes. This is an indication of ordering of the system at sorption process which means that solute molecules allocated in metastable voids of glassy structure lose some degrees of freedom. It is apparently related to restrictions of intermolecular motion of sorbed molecules in the glassy polymer structure. From this viewpoint we may figure out clear distinctions between entropy changes upon bulk sorption in rubbery vs glassy polymer. In the case of equilibrium rubbery structure monomer units are involved in thermal motion and so does the solute molecule which enters the structure in the course of sorption. It means that no restrictions appear for solute rotational or translational movements in the effective lattice of polymer solution. Therefore, noncombinatorial entropy changes are small.

The case of glassy structure is different because thermal motion of monomer units is restricted, and polymer conformations are “frozen”. As the result of such conformational restrictions, a substantial part of polymer, free volume, becomes unavailable for monomer units. This part of nonequilibrium free volume may be considered as metastable voids in glassy structure. According to the theory,<sup>10</sup> the fraction of such voids is given by  $\phi_V^0$ . It is worth emphasizing that metastable voids appear not in addition to the free volume of the rubbery state but as the part of it. Therefore, the total free volume of polymer does not change at glass transition.

In principle, there might be two scenarios of transformation of equilibrium free volume into the metastable voids. One is the gradual increase of their fraction as the temperature decreases below  $T_g$ . Another is the stepwise increase, when substantial fraction of free volume is transformed into metastable voids in the narrow temperature range near  $T_g$ . In both cases, however, the volume of polymer will change continuously with breakpoint at  $T_g$  in accordance with experimental dilation curves in vicinity of glass transition.<sup>6</sup> The data obtained in the present study support the stepwise scenario (see Figure 8). Gradual increase of  $\phi_V^0$  would mean that polymer chain loses mobility unit by unit upon cooling below  $T_g$ , which looks like unrealistic. The process is rather cooperative when many polymer segments become “frozen” more or less simultaneously. In such case all the free volume around these segments becomes “frozen”, too.

Let us then turn back to the sorption of solute molecule in the bulk glassy structure. Metastable void seems to be the best target for the intrusion of the solute molecule into the



**Figure 13.** Influence of molar volume of the solute on entropy depression parameter  $s_{12}$ : 1, fluorinated toluenes; 2, *n*-alkanes; 3, *n*-perfluorooctane.

bulk. Thermodynamically it is preferable because there is no need to put polymer chains apart to make necessary space for the solute molecule. It results in highly negative values of the enthalpy of sorption in the glassy structure. The entropy of sorption is also negative because the solute molecule loses its mobility when allocated in the metastable void. In principle, sorption of solute can cause plasticization of glassy structure and reestablish the mobility. However, the IGC experiment is performed at infinite dilution when solute concentration is close to zero, i.e., very far from the onset of plasticization effects. Thus, the glassy state of the polymer remains, and the sorbed solute molecule get “trapped” in the metastable void, providing negative values of entropy depression parameter  $s_{12}$ .

In terms of presented approach the entropy depression parameter should be sensitive to the molar volume of the solvent. Large molecules should meet more restrictions being allocated in metastable voids, and so the negative values of  $s_{12}$  should increase with the molar volume. Figure 13 presents dependence of  $s_{12}$  on the molar volume of solute molecules. Although the general trend is just as presumed, there are some differences between aliphatic and aromatic solutes.

Fluorinated toluenes demonstrate rather linear dependence of  $s_{12}$  on the molar volume: the larger is the solute molecule, the more negative is entropy depression. Linear regression for fluorinated toluenes is the following:  $s_{12} = -2.84 - 0.53V_m$ . The intercept of linear plot is very close to zero. It has clear physical meaning as solutes with zero molar volume will definitely cause no entropy depression. As no such condition was predefined in the model, we believe this result to be an indication of the adequacy of thermodynamic approach used.

The values of  $s_{12}$  for  $C_7$ – $C_9$  *n*-alkanes and perfluorinated  $C_8$  stay within the linear trend found for toluenes despite the fact that the enthalpy of interaction of these solutes with AF1600 is very different (see  $\chi_H^\infty$  values in Figure 11). On the basis of it, one can assume that the linear trend in Figure 13 is independent of solute–polymer interactions and reveals universal dependence for entropy depression due to geometric restrictions for solute allocation in glassy AF1600. However, alkanes  $C_{10}$ – $C_{16}$  clearly deviate from this characteristic dependence. Starting with  $C_{10}$  the value of  $s_{12} = -104 \pm 10$  J/(mol K) becomes almost independent of molar volume. It does not seem to be the physical limit of  $s_{12}$  for large solute molecules, as more negative value  $-126$  J/(mol K) was found for perfluorotoluene. One can suppose that the reason for such deviation is conformational flexibility of

*n*-alkanes. The estimated contour length of *n*-nonane is 12.1 Å, which is close to Kuhn segment length (doubled persistent length<sup>47</sup>) of the aliphatic chain. Probably, if the length of solute molecule exceeds this value, inner degrees of freedom for conformational motion appear that prevents further increase in negative values of  $s_{12}$ . There is no such effect for rigid conformations of fluorinated toluenes.

## 5. Conclusions

This work is a revisitation of thermodynamic studies of amorphous Teflon AF1600 started about 10 years ago. Many observations made earlier were confirmed. In agreement with the previous results, strong exothermic character of enthalpies of sorption for hydrocarbon solutes was demonstrated. New results indicate that perfluorinated and F-containing compounds are characterized by larger solubility coefficient  $S$  as compared with hydrocarbons. For a series of solutes of the same nature (aliphatic hydrocarbons) a linear correlation between  $\log S$  and  $T_c^2$  is observed.

However, several new results were obtained. For several solutes of the same nature (*n*-alkanes  $C_{13}$ – $C_{16}$ ) it was possible to study the dissolution process both below and above  $T_g$  of the polymer. It was shown that in the vicinity of  $T_g$  a break in the retention diagrams is observed. Enthalpies of sorption below  $T_g$  are markedly more exothermic than in the rubbery state of the polymer. Extrapolation of the linear dependence of  $V_g$  in the rubbery state to the temperatures below  $T_g$  shows that the retention volumes  $V_g$  (or solubility coefficients) of such hypothetical rubbery materials at  $T < T_g$  are smaller by about 2 orders than actually observed  $V_g$  values in the glassy state.

Interesting results were obtained for a series of toluene derivatives with varying content of C–F and C–H bonds. In contrast to the commonly observed trend when the solubility coefficient increases with increasing propensity to condense state (as expressed by  $T_c$  or  $T_c^2$ ) for the series of solutes from  $C_6F_5CF_3$  to  $C_6H_5CH_3$  the  $S$  values decline as  $T_c^2$  increases. It means that the propensity to condense state is not the single factor that determines the solubility of vapor in polymers. A reduction of the  $S$  values of F-containing toluene derivatives as the concentration of F–C bonds decreases can suggest that for every F-containing toluene the data points shown in Figure 5b belong to separate linear increasing correlations with  $T_c^2$  for the series of solutes with the same content of C–F bonds.

The Adamova–Safronov model<sup>10,11</sup> was successfully applied in interpretation of the data gained from IGC experiments. This model for glassy polymer solutions is based on the Flory–Huggins interaction parameter  $\chi$  and glassy state structural parameters: excess free volume  $\phi_v^0$ , polymer cohesion energy  $\epsilon_{22}$ , and entropy depression term  $s_{12}$ . It permits a meaningful physical interpretation of sorption data for various solutes in the polymer studied. In the Flory–Huggins interaction parameter  $\chi$  the enthalpy contribution substantially dominates over the non-combinatorial entropy, which might rather be neglected in thermodynamic analysis. Normal alkanes are very poor solvents for AF1600 with high positive values of enthalpy parameter  $\chi_H^\infty$ . The quality of the solvents (*n*-alkanes) gets worse for the molecules with larger length. The physical reason for this is poor molecular interaction between fluorine atoms of the polymer and hydrogen atoms of *n*-alkanes. This interaction can be substantially improved when hydrogen is substituted by fluorine in solute molecule. Perfluorinated solutes are characterized by negative values of enthalpy parameter  $\chi_H^\infty$ .

Thermodynamic treatment of the sorption data in AF1600 both in rubbery and glassy state showed that below  $T_g$  a fraction (about 12 vol %) of nonequilibrium free volume, which may be considered as metastable voids in polymer glassy structure, governs the thermodynamic behavior of AF1600. It was assumed



that metastable voids appear in a stepwise manner in relatively narrow temperature range in the vicinity of  $T_g$ . In this region transformation of the part of equilibrium free volume of elastic polymer to nonequilibrium state takes place. It is caused by restrictions in the conformational mobility of macromolecular chains.

Sorption of solutes in nonequilibrium free volume has the major effect on the thermodynamics and provides large negative values of partial excess enthalpy and entropy of solute. Enthalpy contribution from the glassy state is independent of the nature of solute and influenced exclusively by cohesion energy of the polymer. On the contrary, entropy of sorption in nonequilibrium free volume is certainly solute-dependent: entropy depression is proportional to the molar volume of the solute but does not depend on the interaction between solute and AF1600. It means that the main reason for entropy depression upon sorption is immobilization of solute molecules located in metastable voids in glassy structure. Internal degrees of freedom of sorbed solute molecules associated mainly with their flexibility can, however, limit entropy depression.

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