Investigation of Polymers by Inverse Gas Chromatography

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Investigation of Polymers by Inverse Gas Chromatography

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S *Supporting Information*

ABSTRACT: This Perspective conveys to the general reader of *Macromolecules* the basic ideas and possibilities of inverse gas chromatography (IGC). This method which appeared about 50 years ago is now a versatile tool for investigation of the interactions of polymers with vapors and study of polymer properties. The focus of this Perspective is on the study of bulk sorption of low molecular weight compounds in polymers. The results of chromatographic determination of solubility coefficients and sorption isotherms as well as the diffusion coefficients of vapors in polymers are discussed. Special attention is paid to the thermodynamic properties of glassy polymers on the phenomena in the vicinity of the glass transition. Information on IGC as a probe method for the determination of free volume in polymers is also presented.
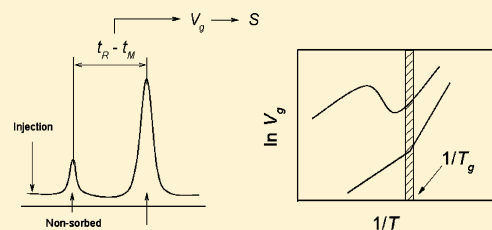
1. INTRODUCTION

Inverse gas chromatography (IGC) is a powerful method for investigation of polymer properties through polymer interaction with low molecular weight compounds. In contrast to analytical chromatography, the aim of IGC is not determination of nature or concentration of the components of some gases or liquids. The common feature of analytical chromatography and IGC is that both methods are dynamic. A principal difference between them is that in IGC a polymer (or other nonvolatile material) is immobilized within a column in the form of stationary phase. This phase is then characterized by monitoring the behavior of known volatile compounds (probes) that are introduced into the column with the stream of carrier gas.

The foundations of IGC were formulated in respect of adsorption on solid inorganic sorbents.[1−3] Interest in polymers as materials of the stationary phases and objects of investigation appeared after Smidsrod and Guillet[4] discovered unusual behavior in retention of organic vapors in the column with poly(*N*-isopropylacrylamide) as the stationary phase below and above the glass transition of this polymer. Much attention to such phenomena, to bulk sorption and surface adsorption in polymers, became evident in subsequent years. Now IGC is a reliable source of information on absorption and adsorption in polymers and on polymer properties. Numerous reviews and several books have been written on IGC.[5−19] Some of them were published 20−40 years ago.[5−9] Though being brilliant[5] or simply useful, today they are rather outdated. In the 21st century researchers returned many times to the subjects of IGC.[10−19] A special book[10] was published dealing with general questions of IGC. It should be noted that most of those reviews focused on such subjects as polymer surface studies and polymer blends,[11,14,15,18] determination of T_g and other properties of polymers,[13,19] investigation of surfactants, pharmaceuticals,[18] and fibers.[11,12] Meanwhile, some important issues did not receive proper attention in the existing literature, for example, thermodynamics

of glassy polymers, IGC as a probe method for investigation of free volume in polymers, and some others.

In this Perspective we want to focus instead on bulk properties of polymers studied using IGC and very useful for the investigators active in membrane science. The main attention will be on absorption thermodynamics, solubility coefficients and diffusivity of low molecular mass compounds in polymers, and behavior of polymers above and below T_g. All this is important for gas and vapor separation using polymeric membranes, and IGC provides a valuable possibility to investigate membrane materials.

2. BACKGROUND

The method of IGC is based on the measurement of the retention times of probes injected into the column that contains the polymer film under investigation as immobile phase. This retention time should be corrected because it includes the contribution that is necessary for passage of a nonretained component between the point of injection and the detector, i.e., the passage through so-called "dead volume" of the system. Hence, the genuine retention time t_R that is determined by probe's sorption thermodynamics is the difference between the observed retention time of the probe and that of nonsorbing component as is illustrated in Figure 1. Air or methane often serves as such nonsorbing components.

Different symbols are used for the parameters shown in this figure. Here, t_R and t_M are the retention times of retained solute (under investigation) and nonsorbed component, respectively. V_g is the specific retention volume. Some authors design this as V_w (a retention volume reduced to weight of condensed phase in chromatographic column). ΔH_S is the enthalpy of sorption. Other symbols for this quantity are as follows: ΔH_1^S, $\Delta \bar{H}_{1,\text{sorp}}$,
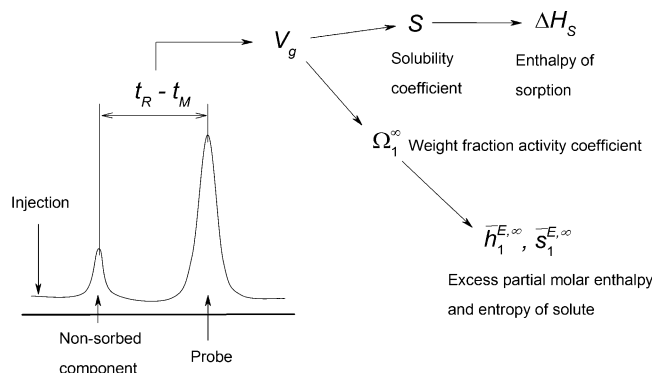
Figure 1. Principles of IGC. For explanations, see the text.

$\Delta H_{1,\text{sorp}}$. The weight fraction activity coefficient Ω_1^∞ is also sometimes denoted by $(a_1/w_1)^\infty$. Excess partial parameters of solutes are expressed in the literature also by different ways, namely for enthalpy, ΔH_1^∞, $\Delta \bar{H}_1^\infty$, ΔH_m^∞, and ΔH_m, and in a similar manner for entropy and free energy.

The main aim of sorption measurements including IGC is an estimation of the equilibrium partition constant K_C of a probe between gaseous and liquid (or polymeric) phases.[20] On the one hand, for the system attaining an equilibrium, it can be expressed as the ratio of concentrations of the probe in the liquid phase (c_L) and in the gaseous phase (c_G):

$$K_C = \frac{c_L}{c_G} \tag{1}$$

Provided sorption takes place in the bulk of the polymer film (we shall see that this is not always the case), the partition constant K_C determines the main observed quantity of IGC, the specific retention volume V_g. Figure 1 in a qualitative manner illustrates that all the main thermodynamic parameters can be obtained via V_g. It can be added that some other important parameters such as the Flory−Huggins parameter χ and the solubility parameter δ can be also deduced via V_g. Thus, for the probe that acts as an ideal gas and when pressure gradient in the column can be neglected

$$K_C = \frac{V_g T}{273} = \frac{V_N}{w} \tag{2a}$$

where V_g is the retention volume (cm^3/g) reduced to 273 K, V_N is the neat retention volume defined as $V_N = F_c(t_R - t_M)$, where F_c is the flow rate of carrier gas, and w is the mass of polymer sorbent in the column. Equation 2a implies that the specific retention volume is corrected to the standard temperature 0 °C. Such procedure was widely used since pioneer works like refs 4 and 5. It was included into official recommendations of IUPAC[21] and is still employed in the current works (see e.g. ref 11). However, later it was noted[22−24] that this procedure is not justified. In subsequent works by Davankov[25,26] that were taken as the basis for the novel official IUPAC recommendation, a different definition of the specific retention volume was proposed via the formula

$$V_g^{273} = \frac{273.2}{T_{\text{col}}} V_g \tag{2b}$$

where V_g^{273} is the specific retention volume determined at T_{col}. Hence, the reduced specific retention volume V_g^{273} turns out to be lower than the specific retention volume V_g as column temperature T_{col} increases. The difference is bigger at higher

temperatures, while at 35 °C the difference is less than 10%. It must be admitted though that the majority of researchers do not follow this novel approach as can be judged from the literature. Still this subject requires further consideration.

If the sorption isotherm obeys Henry's law

$$C = Sp \tag{3}$$

then the solubility coefficients S can be estimated by means of IGC. Apparently, Kawakami and Kagawa first proposed[27] to calculate the solubility coefficients using a simple formula

$$S = V_g \rho / p^0 \tag{4}$$

Here $p^0 = 1$ atm is the standard pressure (or outlet pressure) of the column and ρ is the density of the polymer. Accordingly, S can be presented using the traditional units cm^3 (STP)/cm^3 atm.

We shall consider in more detail the estimation of the solubility coefficients by the IGC method in section 4.

The temperature dependence of the specific retention volume V_g allows one to calculate the enthalpy of sorption ΔH_S:

$$\Delta H_S = -R \frac{\text{d} \ln V_g}{\text{d}(1/T)} \tag{5}$$

Some researchers proposed[28] to consider the changes of inner energy U_1^S instead of enthalpy of sorption ΔH_S. Since $\Delta H_S = U_1^S + RT$, at typical temperature of chromatographic experiment about 400 K, the correction RT is about 3 kJ/mol, i.e., small in comparison with the reported ΔH_S values.

In the conditions of the infinite dilution the specific retention volume can be related to the important characteristics of real solutions in polymer phases, activity coefficient γ_1^∞ (here 1 indicates that it refers to the solute and upper index (∞) reminds that this value characterizes the infinite dilution). This parameter is defined as the ratio of activity a_1 and mole fraction x_1, while the activity $a_1 = f_1/f_1^0$, that is, the ratio of the fugacity in the polymer and in the standard (liquid) state of the solute. The following equation holds[29−31] for the mole fraction activity coefficient γ_1^∞

$$\ln \gamma_1^\infty = \ln \left(\frac{273.2R}{V_g p_1^0 M_2} \right) - \frac{p_1^0}{RT}(B_{11} - V_1) \tag{6}$$

where p_1^0 is the saturated vapor pressure of the solute at T, V_1 is its molar volume, B_{11} is the second virial coefficient, and M_2 is the molecular mass of the stationary phase. Note that this equation was obtained for classical gas liquid chromatography, that is, for relatively low molecular mass of the stationary phase. This equation can also include additional terms that account for compressibility and interaction of solutes with carrier gas.[5]

It has been noted[32] that use of eq 6 in the case of IGC of polymers meets some problems. The molecular mass M_2 can be either unknown or poorly defined; it is not clear which of the number-average M_n or weight-average M_w should be used, how to work with cross-linked polymers. This problem was overcome in a treatment by Patterson et al.[32] These authors suggested to use instead weight fraction activity coefficient $(a_1/w_1)^\infty$, defined as the ratio of activity a_1 to weight faction w_1, so eq 6 can be rewritten as

$$\ln \Omega_1^\infty = \ln \left(\frac{a_1}{w_1} \right)^\infty = \ln \left(\frac{273.2R}{V_g p_1^0 M_1} \right) - \frac{p_1^0}{RT}(B_{11} - V_1) \tag{7}$$

where M_1 is the molecular weight of the solute. In this way, a possible dependence of $(a_1/w_1)^\infty$ on M_2 can be included in the

experimentally observed V_g values. Hence, namely this equation is mainly used in inverse gas chromatography of polymers.

Using these activity coefficients, it is possible to define the partial molar thermodynamic parameters of mixing, namely Gibbs free energy of mixing $\overline{g}_1^{E,\infty}$

$$\overline{g}_1^{E,\infty} = RT \ln\left(\frac{a_1}{w_1}\right)^{\infty} \tag{8}$$

and partial molar enthalpy $\overline{h}_1^{E,\infty}$ and entropy $\overline{s}_1^{E,\infty}$ of mixing:

$$\overline{h}_1^{E,\infty} = R\frac{\partial \ln\left(\frac{a_1}{w_1}\right)^{\infty}}{\partial(1/T)} \tag{9}$$

$$\overline{s}_1^{E,\infty} = \frac{\overline{h}_1^{E,\infty} - \overline{g}_1^{E,\infty}}{T} \tag{10}$$

Using eq 8, it is possible to estimate the Flory–Huggins parameter χ. At relatively large molecular mass M_2 and in the conditions of infinite dilution

$$\chi = \ln\left(\frac{273.2Rv_2}{V_g p_1^0 v_1}\right) - 1 - \frac{p_1^0}{RT}(B_{11} - V_l) \tag{11}$$

where v_1 and v_2 are the specific volume (cm^3/g) of the polymer and the solute, respectively. The Flory–Huggins parameter is the measure of noncombinatorial free energy of interaction of solutes with the polymer. It is often presented as the sum

$$\chi = \chi_H + \chi_S \tag{12}$$

where the term χ_H is related to the solubility parameter δ_2 of the polymer.[5]

Other thermodynamic properties that characterize intermolecular interactions were extensively investigated by means of IGC; however, they are not considered in this Perspective. Detailed information on those issues can be found in the literature (see e.g. refs 5, 6, 11, and 15).

So far we have discussed the processes of bulk sorption in chromatographic columns. Meanwhile, for the same polymer–solute pair depending on temperature and polymer film thickness the processes of adsorption on phase boundaries can play important roles. Retention of solutes can be sensitive also to the processes on interfaces. Apparently, for the first time it was noted as early as in 1961 by Martin.[33] Later it was Berezkin et al.[34−36] and Conder et al.,[37] who considered in a more systematic way the role of retention on different interfaces. In the most general case, the net retention volume can be presented as the sum of several contributions:

$$V_N = K_L V_L + K_{GL} S_{GL} + K_L K_{LS} S_{LS} \tag{13}$$

where K_L is the absorption partition constant, K_{GL} and K_{LS} are adsorption partition constants on the interface gas–liquid (polymer) and liquid–solid, respectively, and S_{GL} and S_{LS} are corresponding surface areas.

Initial stage of IGC investigation of bulk sorption must include special tests that would indicate possible contribution of surface adsorption in the observed retention. The procedure of such tests is well developed. Experiments with different loading (mass of the polymer phase in the column) allow one to recognize a difference between completely prevailing bulk absorption and a contribution of surface adsorption.

The linear dependence of V_N versus w that proceeds from the origin of coordinate is an indication of the absence of any role of

surface adsorption (Figure 2). Otherwise, it is possible to consider independence of V_g versus w bearing in mind that $V_g = V_N/w$.
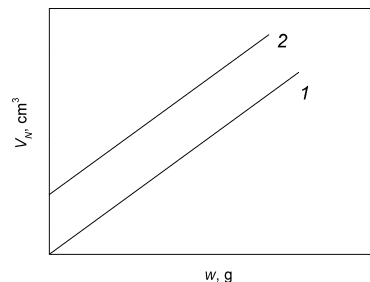
Figure 2. Dependence of V_N versus w. Case 1: completely bulk sorption; case 2: mixture of bulk sorption and surface adsorption.

3. POLYMERS ABOVE AND BELOW THE GLASS TRANSITION TEMPERATURES

Retention Diagrams. The main part of the results obtained using the IGC method refers to the polymers above their glass transition temperature T_g. This was predetermined by the classical work by Smidsrod and Guillet,[4] who studied temperature dependences of the specific retention volume of several organic solutes in poly(N-isopropylacrylamide) (PNIPAM). It was found that good solvents of this polymer (n-butyl alcohol and acetic acid) revealed linear dependences of $\ln V_g$ versus $1/T$ (retention diagram) both below and above the glass transition temperature, while nonsolvents (hydrocarbons) exhibit strongly nonlinear (Z-shaped) retention diagrams shown in Figure 3.
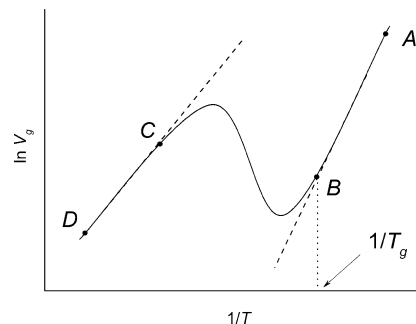

Figure 3. Schematic view of retention diagram in passing through glass transition of a polymer.

It was further assumed that the low-temperature part of the Z-shaped retention diagrams corresponds only to surface adsorption as the mechanism of retention, while above some temperature nonequilibrium part of the diagram takes place. At further increase in temperature bulk sorption prevails, and the linear, high temperature part of the diagram has a slope that corresponds to the enthalpy of absorption ΔH_S.

Originally, it was supposed that nonsolvents cannot penetrate inside the polymer film, so the Z-shaped retention diagram is observed only for the systems "glassy polymers–nonsolvents". However, even the works that appeared in 1970s showed that Z-shaped retention diagrams can be observed also with good solvents as IGC solutes (e.g., atactic polypropylene–hydrocarbons[38]), whereas surface adsorption can also prevail even above T_g when polyacrylonitrile is used as chromatographic phase.[39] Further studies indicated that the form of retention

diagrams (linear or Z-shaped) can depend on various factors such as nature of support, carrier gas flow rate, and the thickness of polymer film.[6,13,40,41] Z-shaped retention diagrams were observed for numerous glassy polymers and copolymers.[40,42–44]

The role of the diffusion limitations was visually demonstrated by Braun and Guillet[45] (Figure 4). It is seen that when the
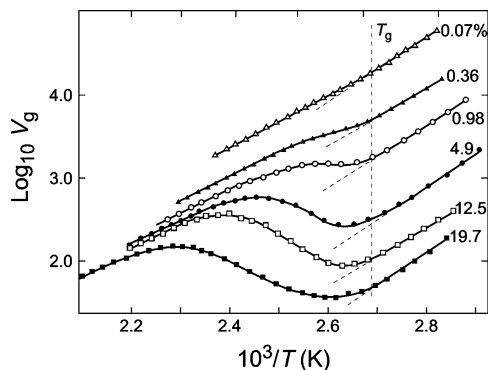
Figure 4. Retention diagrams of the system *n*-hexadecane−polystyrene with different contents of the polymer phase in the column. Reproduced with permission from ref 45.

thickness of the polymer layer in the column becomes smaller, the Z-shaped character of the retention diagram is less pronounced, and at a very small loading the dependence of log V_g versus $1/T$ becomes nearly linear. However, the slopes of the dependences at lower temperatures of the diagrams, where surface adsorption prevails, were not constant, so the enthalpy of adsorption depended on the loading of the polymer, a strange observation that required an explanation.

As has been discussed by Nesterov[6] in the temperature range where retention is realized via surface adsorption and in the nonequilibrium region of the Z-shaped retention diagrams, the chromatographic peaks are strongly asymmetric (have long "tails"). This is related to diffusion limitations due to the relatively low diffusion coefficients. The original semiquantitative model for a description of the chromatographic behavior in vicinity of T_g was proposed by Braun and Guillet.[5] Later, a more sophisticated model proposed by Davis et al.[41] aimed to take into account the shape of the peaks and describe both bulk and surface adsorption effects. A feature of this model is that in addition to classical retention times another parameter,

dimensionless average solute elution time (dimensionless first moment μ), is used for asymmetric peaks.

Thus, the form of the retention diagrams does not allow one to distinguish between the behavior of rubbery and conventional glassy polymers. The former states of materials are characterized by linear dependence of log V_g versus $1/T$ with positive slopes (negative enthalpy of sorption). Numerous examples of such retention diagrams are available in the literature, and some examples can be found in refs 46−49.

It was found that polymers with increased free volume or enhanced diffusion coefficients revealed linear dependences of log V_g both above and below T_g. It is important that in such polymers bulk sorption prevails not only at high temperatures but also in the glassy state. The first example of such behavior was glassy poly(vinyltrimethylsilane).[50,51] Later, numerous polymers with large free volume demonstrated the same behavior: prevailing of bulk sorption mechanism of retention in glassy state, absence of Z-shaped retention diagrams for both solvents and nonsolvents.[52–57] Chemically, this group of polymers important as membrane materials includes glassy polymers with bulky side groups like $Si(CH_3)_3$, amorphous glassy perfluorinated copolymers, polymers of inner microporosity (PIMs), and thermally rearranged polymers. Their fractional free volume (FFV) is greater than 20%; hence, according to the free volume model they are characterized by larger diffusion coefficients of various solutes.

If the temperature range studied included the glass transition temperature, then the break of the slope of linear retention diagrams can be often observed in the vicinity of T_g:[52] the steeper dependences of V_g (more negative enthalpies of sorption) were observed at lower temperatures (Figure 5).

These high free volume glassy polymers are distinguished by many unusual properties which will be considered in the following sections in comparisons with those of rubbery polymers. It can be added that breaks of linear dependence of log V_g versus $1/T$ have been observed also for other systems, e.g., for poly(methyl methacrylate).[60]

Enthalpy of Sorption and Partial Molar Enthalpy of Mixing. Enthalpies of bulk sorption of different hydrocarbons in glassy polymers found using the eq 5 are presented in Table 1, where they are compared with those of several rubbery polymers. It is seen that absorption in glassy polymers is much more exothermic as compared with the same process in polymers above their T_g.
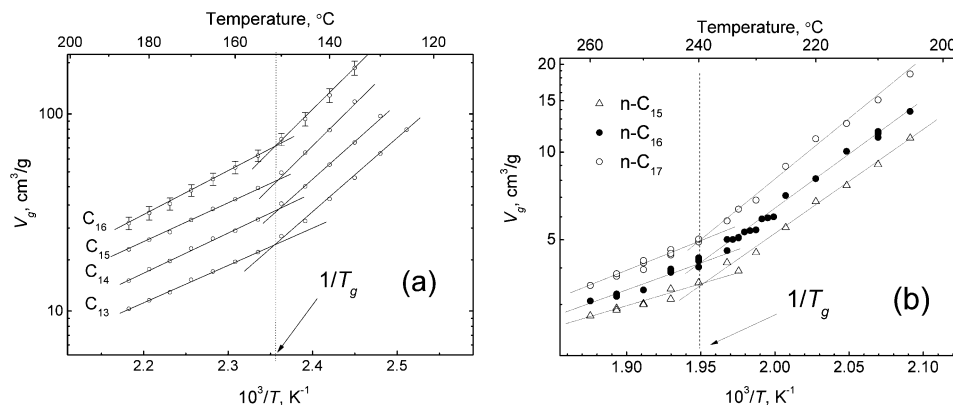
Figure 5. Retention diagrams of *n*-alkanes C_{13}−C_{17} in amorphous Teflons AF1600 (a) and AF2400 (b) (random copolymers of perfluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (65 mol % of the comonomer in AF1600 and 86 mol % in AF2400)).[58,59] Part (a): reproduced with permission from ref 58.

Table 1. Enthalpy of Sorption ($-\Delta H_S$, kJ/mol) of *n*-Alkanes in Glassy and Rubbery Polymers

solute	glassy polymers[a]			rubbers or polymers above T_g[b]				
	PVTMS[51]	addition PTMSN[53]	PIM-1[54]	PDMS[61]	MTFP- siloxane[62]	PSiMe[63]	PPM[49]	PC[64]
C_3H_8	26.8	29	42.8			13.4	21.2	
C_4H_{10}	33.4	36	51.3	20.4		19.9	23.5	
C_5H_{12}	39.1	37	61.0	24.1	22.1	24.4	27.7	
C_6H_{14}	44.7	44	63.8	28.2	25.7	28.5	31.2	
C_7H_{16}	36.1	49	68.7	32.3	29.6	31.9	36.0	
C_8H_{18}	33.4	51	80.0	36.6	34.1		40.5	
C_9H_{20}	38.7	56	87.1	40.8	38.1		45.1	21.8
$C_{10}H_{22}$	43.7	61	88.1	45.9	42.0		48.8	24.5
$C_{11}H_{24}$		66		48.1	46.0			30.9

[a]PVTMS = poly(vinyltrimethylsilane); addition PTMSN = additive poly(trimethylsilylnorbornene); PIM-1 = polymer of intrinsic microporosity.
[b]PDMS = polydimethylsiloxane; MTFP siloxane = polysiloxane with methyl and trifluoropropyl side groups; PSiMe = polysilmethylene; PPM = polypentenamere; PC = polycarbonate.

In some cases the difference of the ΔH_S values for the same solute can reach up to 40 kJ/mol. An interesting trend was observed for PVTMS. For smaller solutes absorption in this polymer is more exothermic than in rubbers. However, starting from some size of the solute molecule the ΔH_S values in PVTMS and rubber become similar. It was interpreted[51] that for smaller solutes the bulk sorption involves a sort of condensation of sorbed molecules into preexisting holes in the polymer. Starting from some size of the solutes, accommodation of hydrocarbons into preexisting holes becomes hindered, so dissolution takes place in the more dense matrix like in rubber, and this is reflected in the values of ΔH_S.

Such mechanism is better understood in considering the partial molar enthalpies of mixing $\overline{h}_1^{E,\infty}$ that are included in the formula

$$\Delta H_S = \overline{h}_1^{E,\infty} + \Delta H_C \qquad (14)$$

where ΔH_C is the enthalpy of condensation equal to $(-\Delta H_v)$, enthalpy of evaporation. According to this equation, the process of vapor sorption can be considered (in terms of the Hess cycle) as the sequence of the two stages: a transition from vapor to condensed phase of the solute in the condition of infinite dilution and mixing with the polymer matrix. The thermodynamic parameters ΔH_C has nothing to do with the polymer nature and its physical state. It is the properties of solutes, and they are tabulated in the handbooks.[65] On the other hand, all the interactions between the solute molecule and the polymer are reflected in the term $\overline{h}_1^{E,\infty}$. So the analysis of this parameters is useful for understanding sorption mechanism.

An important feature of glassy polymers with high free volume is usually observed exothermic character of mixing in these polymers. It is illustrated by the data of Table 2, which should be compared with Table 3, where the data for polymers above their glass transition temperature are given.

Table 2 indicates that the process of mixing in glassy polymers is strongly exothermic. In addition, the $\overline{h}_1^{E,\infty}$ values are strongly sensitive to the size of solute molecules. On the other hand, in the polymers above their T_g the process of mixing is endothermic or is characterized by small negative $\overline{h}_1^{E,\infty}$ values. No influence of the size of solute molecules is observed here.

Another feature of glassy polymers with large free volume is also negative values of excess entropy of mixing that can be found using eq 10 where the excess free energy of mixing $\overline{g}_1^{E,\infty}$ is defined according to eq 8. The correlation of $\overline{h}_1^{E,\infty}$ and $\overline{s}_1^{E,\infty}$ for a glassy polymer and two rubbers is shown in Figure 6. It is evident that a more exothermic mixing of the solutes leads to a more significant

Table 2. Excess Enthalpies of Mixing $-\overline{h}_1^{E,\infty}$ (kJ/mol) in Glassy Polymers

solute	V_c (cm³/mol)	PVTMS[51]	addition PTMSN[53]	PIM-1[54]
n-C_4H_{10}	255	13.8	13.7	21
n-C_5H_{12}	311	14.2	11.3	26
n-C_6H_{14}	368	18.4	15.3	28
n-C_7H_{16}	426	7.9	17.4	30
n-C_8H_{18}	486	1.7	16.7	38
n-C_9H_{20}	543	−2.9	21.7	40
cyclohexane	308	7.5	9.0	
benzene	260	10.9		25

Table 3. Excess Enthalpies of Mixing $\overline{h}_1^{E,\infty}$ (kJ/mol) in Polymers above Their T_g

solute	PDMS	natural rubber[66]	PPM[49]	poly(p-chlorostyrene)[67]
n-C_4H_{10}	1.9[61]	−0.6	−1.3	
n-C_5H_{12}	1.6;[61] −0.2[66]	−3.0	−1.5	1.4
n-C_6H_{14}	0.5; 1.2[66]	0.8	−1.1	4.0
n-C_7H_{16}	−0.8;[61] −1.2[66]	−0.4	−1.6	1.9
cyclohexane	−0.7[61]		−1.0	
benzene	2.5[61]			3.6
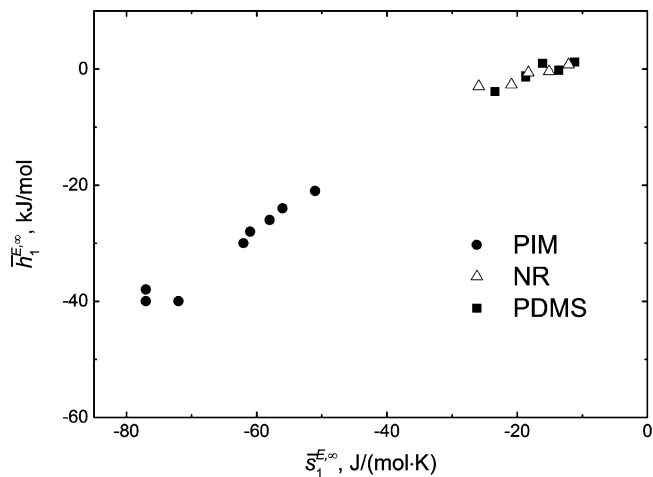
Figure 6. Correlation of $\overline{h}_1^{E,\infty}$ and $\overline{s}_1^{E,\infty}$ in a glassy polymer (PIM-1)[54] and two rubbery polymers: natural rubber and PDMS.[66]

loss in the translational degrees of freedom, which is expressed in quite negative values of $\overline{s}_1^{E,\infty}$.

Similar behavior was observed for other glassy polymers.[51−53] Note that in the case of a glassy polymer the values of $\overline{h}_1^{E,\infty}$ and $\overline{s}_1^{E,\infty}$ always vary over a wide range. In contrast, for rubbers the chemical structure of the solutes has little effect on the mixing parameters. The positive slope of the correlation shown in Figure 6 indicates that for more exothermic mixing greater limitations are observed in inner degrees of freedom (inner rotation, conformation transitions, etc.) that are manifested in the $\overline{s}_1^{E,\infty}$ values. There are also many examples of similar correlations between the partial molar enthalpy and the entropy of mixing for solutions of low molecular mass organic compounds.[68]

It can be added that other reasons can explain strong negative enthalpy of mixing, for example hydrogen bonding. Thus, it was shown[69] that the $\overline{h}_1^{E,\infty}$ values for the systems (water vapor)-regenerated cellulose and its derivatives can be characterized by the $\overline{h}_1^{E,\infty}$ values −18.5 kJ/mol or even −31.8 kJ/mol.

Highly permeable glassy polymers (especially PTMSP) have a disadvantage: they are prone to fast aging which is revealed in decreases in free volume, permeability,[70,71] and chromatographic parameters (elution order of compounds, peak symmetry, retention times).[72] It has been shown[71] that three different mechanisms can be involved in aging of PTMSP: (1) physical aging (contraction of polymer matrix), (2) adsorption aging (sorption of aerosols, e.g., vacuum oil), and (3) chemical aging (oxidation of double bonds with formation of carbonyls). For PTMSP phase in inert atmosphere of chromatographic column the mechanisms 2 and 3 are unlikely and probably mechanism 1 prevails. It complicates not only the studies of such polymers using the IGC method but also their analytical applications[72] because the observed retention times become variable.

Sorption in Polymers below and above T_g and Thermodynamics of Liquid Solutions. Ample data on dissolution of low molecular mass compounds in polymers above their T_g and some limited set of the data on bulk sorption in glassy polymers allow one to make a comparison with the numerous results of the study of sorption thermodynamics of organic compounds[73,74] and gases in liquids.[75] Different solvents can be divided into two classes. The first class is represented by solvents whose molecules are nonpolar and characterized by nondirected and nonsaturated interaction forces (hydrocarbons, weakly polar organic liquids). The second class includes liquids with more or less ordered inner structure with a tendency to formation of associates. It is represented by water, lower alcohols, and some organic compounds (nitriles). The associated liquids, and water first and foremost, are characterized by large negative entropy and enthalpy of mixing (dissolution) which are sensitive to the size of dissolved molecules, while athermal mixing and weaker entropy effects are characteristic for hydrocarbons. In this regard, as is discussed in more length elsewhere,[76] the effects of solute size on the partial molar parameters of mixing with glassy polymers permit one to speak about similarity to associated solvents (water, lower alcohols), while the polymers above the glass transition temperature exhibit behavior similar to unstructured liquids, such as aliphatic hydrocarbons. In both systems (rubbery polymers and liquid hydrocarbons) the elementary act of dissolution involves the overcoming the work of displacement of chains of "the solvent". This process is absent in glassy polymers and associated liquids, so the mixing process is exothermic provided a solute molecule can be accommodated into a microcavity (area with decreased density). So, it is possible to speak on substitutional solutions in rubbers

and liquid hydrocarbons and interstitial solutions in water and glassy polymers. Note that interstitial solutions (dislocation filling effects) are especially common in solid solutions (alloys)[77] where the size of the solute atom has a critical importance.

Thermodynamics of Sorption above and below Glass Transition Temperature of Polymers. The retention diagrams and enthalpy of sorption discussed above can be considered as a manifestation of polymer behavior in the vicinity of their glass transition temperature. Understanding the nature of the sorption phenomena occurring in passing through the glass transition temperature is the main goal of several models proposed. Unfortunately, the Flory−Huggins model,[78,79] UNI-FAC model by Fredenslund et al.[80] modified by Oishi and Prausnitz[81] known as UNIFAC-FV (see, for instance, refs 82 and 83), the group-contribution lattice-fluid equation of state (GCLF-EoS),[83,84] and a pseudo EoS model by Ruzette and Mayes[85,86] do not take into account the terms being influenced by glassy nature of polymer. However, there are models that are seemingly capable to describe sorption data below T_g. Thus, in attempt to consider a complicated nature of glassy polymer matrix, Vrentas and Vrentas[87] derived a quite lengthy expression for the solubility coefficient in a glassy polymer:

$$\ln S = -(\ln p_1^0) - \ln\left(\frac{M_1 V_1^0}{22400}\right) - (1 + \chi)$$
$$- \frac{M_1(C_p - C_{pg})A}{R}\left(\frac{1}{T_{g2}} - \frac{1}{T}\right) \tag{15}$$

where C_p and C_{pg} are specific heat capacities at constant pressure for the equilibrium liquid and glassy polymer, respectively; T_{g2} is the glass transition temperature of the neat polymer; A is the coefficient in the equation $T_{gm} = T_{g2} - Aw_1$, where the glass transition temperature T_{gm} corresponds to the solute−polymer mixture at sufficiently low solute concentrations w_1. The following formula holds for the enthalpy of sorption:

$$\Delta H_S = -RT^2 \frac{\partial p_1^0}{p_1^0 \partial T} - RT^2 \frac{\partial \chi}{\partial T} - M_1(C_p - C_{pg})A \tag{16}$$

For a rubbery polymer, the enthalpy of sorption is given by the first two terms of eq 16. The Vrentas−Vrentas model is in agreement with experimental sorption data for polycarbonate−carbon dioxide system at 35 °C[87] and temperature dependence of the partition constants determined by IGC for methanol−poly(methyl methacrylate), methanol−poly(p-methylstyrene), and ethyl acetate−poly(p-methylstyrene).[88,89] A disadvantage of this model is a difficulty of its applications because of numerous parameters needed which are absent for most polymers. In addition, the empirical coefficient A has no evident physical meaning.

Another approach was proposed by Leibler and Sekimoto,[90] who noticed that the key feature of glassy polymers in comparison with rubbery ones is their elastic properties. Excess sorption in glassy polymer was demonstrated to be simply related to the bulk modulus of the glass. The solubility coefficient at low-pressure limit can be expressed as follows:

$$\ln S = -\ln p_1^0(T) - (1 + \chi) - \frac{V_1 K_{gl}^0}{k_B T}\log \varphi_g(T) \tag{17}$$

where K_{gl}^0 is the additional contribution to the bulk modulus which results from the stiffening of the system at the glass
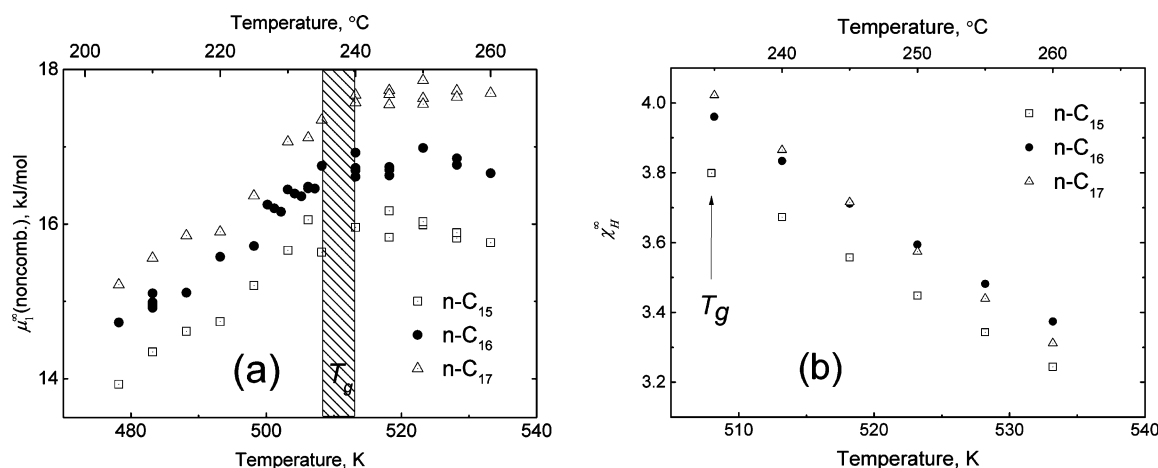
Figure 7. Temperature dependencies of excess chemical potential (a) and enthalpy part of Flory−Huggins parameter (b) of C_{15}−C_{17} n-alkanes in AF2400.
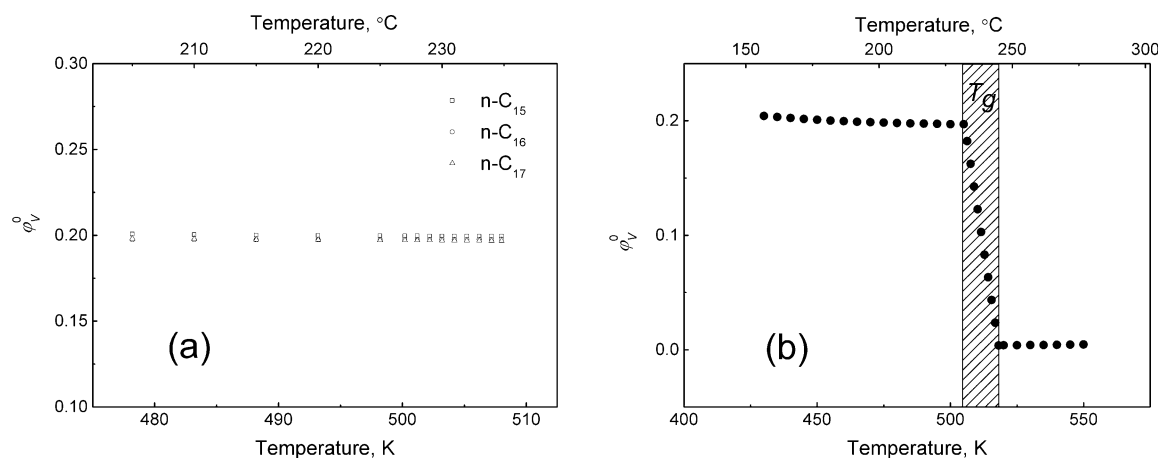
Figure 8. Temperature dependencies of volume fraction of nonequilibrium voids at $T < T_g$ for all solutes (a) and above and below T_g for averaged φ_V^0 (b).

transition, k_B is the Boltzmann constant, and $\phi_g(T)$ is the solute's concentration that causes the isothermal glass transition at temperature T. The authors successfully tested their model for poly(vinyl chloride)−vinyl chloride system at different temperatures. Unfortunately, the Leibler−Sekimoto approach did not find a wide usage.

Recently, for the interpretation of the retention diagrams of n-alkanes in perfluorinated copolymer AF1600 (see Figure 5a) below the glass transition temperature the Adamova−Safronov model[91,92] was applied.[58] Here a similar procedure was realized for another amorphous perfluorinated copolymer Teflon AF2400 (Figure 5b).

Let us consider the implications of the use of this model and IGC data for polymer properties below and above T_g using the AF2400 copolymer as an example. According to eq 18 (an analogue to eq 11), the temperature dependence of the excess chemical potential $\Delta\mu_{1,\text{noncomb}}^\infty$ for solutes can be estimated (Figure 7)

$$\frac{\Delta\mu_{1,\text{noncomb}}^\infty}{RT} = \chi^\infty = \ln\left(\frac{RT}{V_g p_1^0 M_1}\right) - \frac{p_1^0}{RT}(B_{11} - V_1)$$
$$- \left(1 - \frac{1}{r}\right) \tag{18}$$

where r is the degree of polymerization. Here, the left-hand side of eq 18, $\Delta\mu_{1,\text{noncomb}}^\infty$, accumulates all the noncombinatorial contributions into the chemical potential of the solute at infinite dilution. Above T_g, it slightly depends on the temperature whereas below T_g $\Delta\mu_{1,\text{noncomb}}^\infty$ gradually decreases with decreasing temperature.

Noncombinatorial chemical potential of the solvent is considered[91,92] as the sum of two contributions:

$$\Delta\mu_{1,\text{noncomb}} = \Delta\mu_{1,\text{res}} + \Delta\mu_{1,\text{gl}} \tag{19}$$

Here, the residual term $\Delta\mu_{1,\text{res}}$ accounts for molecular interaction in the solution and $\Delta\mu_{1,\text{gl}}$ does for the nonequilibrium state of glassy polymers. According to this theoretical approach, noncombinatorial chemical potential of the solute at infinite dilution can be expressed as follows:

$$\frac{\Delta\mu_{1,\text{noncomb}}^\infty}{RT} = \chi^\infty + \frac{\varepsilon_{22} - Ts_{12}}{RT}(1 - 2\phi_V^0) \tag{20}$$

where ε_{22} is the cohesion energy of the polymer, s_{12} is the entropy depression parameter, and φ_V^0 is the volume fraction of nonequilibrium voids in the initial polymer structure.

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 the basic thermodynamic equations:

Table 4. Entropic Parameters of Sorption of C_{15}–C_{17} n-Alkanes in AF2400

| | $\overline{s}_1^{E,\infty}$ | χ_S^∞ | | $\overline{s}_1^{E,\infty}$ | s_{12} (J/(mol K)) | |
solute	rubbery (J/(mol K))	per mole of solutes	per mole of polymer units	glassy (J/(mol K))	per mole of solutes	per mole of polymer units
C_{15}	−2 ± 6	−0.29	−0.11	−65 ± 5	−109	−42
C_{16}	2 ± 5	0.01	0.00	−66 ± 3	−111	−40
C_{17}	4 ± 5	0.48	0.16	−71 ± 6	−120	−41

$$\overline{h}_1^{E,\infty} = \frac{\partial(\Delta\mu_{1,noncomb}^\infty/T)}{\partial(1/T)} = RT\chi_H^\infty + \varepsilon_{22}(1 - 2\phi_V^0) \qquad (21)$$

$$\overline{s}_1^{E,\infty} = \frac{\partial\Delta\mu_{1,noncomb}^\infty}{\partial T} = -R\chi_S^\infty + s_{12}(1 - 2\phi_V^0) \qquad (22)$$

The Adamova−Safronov model postulates that in rubbery state of the polymer second terms of right-hand parts of eqs 19−22 is equal to zero. So, the enthalpic part of Flory−Huggins parameter can be calculated (Figure 7b). Recently,[58] the temperature dependencies of χ_H^∞ for each solute were approximated by the square equation as follows

$$\chi_H^\infty = a + bT + cT^2 \qquad (23)$$

where a, b, and c are constants. The magnitudes of the enthalpic part of χ^∞ are quite high and are typical for hydrocarbon−fluorocarbon systems (see for instance refs 58, 93, and 94). Assuming that nature of intermolecular interactions in the solute−polymer system is not changed in passing through T_g, one can estimate χ_H^∞ parameter below glass transition based on eq 23. The cohesive energy of polymer ε_{22} of AF2400 was calculated according to the procedure described elsewhere.[58] Then, bearing in mind that cohesive energy of AF2400 is about −21.2 kJ/mol, and using eq 21 one can evaluate temperature dependence of volume fraction of nonequilibrium voids (Figure 7). Surprisingly, for all solutes, φ_V^0 is almost similar and slightly increases as temperature decreases. In the temperature range above T_g, AF2400 is in its equilibrium rubbery state, and its structure contains no nonequilibrium voids ($\varphi_V^0 = 0$); i.e., empty volume[95] in rubbery polymer has fluctuation nature. Below T_g, a part of the empty volume is transformed into nonequilibium state; in other words, it is included into the "frozen" parts of polymer chains. The average value of φ_V^0 in AF2400 is about 0.20.

Values of χ_S^∞ normalized to the effective molar volume of AF2400 repeat unit (Table 4) are close to zero or slightly negative, which indicates that some disordering takes place during sorption of alkanes in AF2400 at $T > T_g$. The absolute values of χ_S^∞ do not exceed 0.16, which is by at least 1 order of magnitude lower than χ_H^∞ values for the same solutes given above (Figure 7b). It means that enthalpy contribution to Flory−Huggins parameter substantially dominates over entropy.

The excess partial molar entropy $\overline{s}_1^{E,\infty}$ of solutes in rubbery AF2400 is close to zero (Table 4). On the other hand, in the glassy state of AF2400 this parameter becomes strongly negative, and this is typical for other glassy polymers with high free volume (see discussion of Figure 6). Consequently, the parameter s_{12} (depression entropy at $T < T_g$) 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.

In relation to the models based on equations of states, the nonequilibrium lattice fluid (NELF) model developed by Dogheri and Sarti[96] should be noted. The NELF model extends

the Sanchez−Lacombe equation of state[97] to the nonequilibrium domain of the glassy polymers and allows the calculation of solubility isotherms in glassy polymer, once the lattice fluid parameters (T^*, P^*, ρ^*) of polymer (2) and solute (1) are available, in addition to polymer density ρ_2^0 in the glassy phase. In the limit of infinite dilution, solubility coefficient of solute is expressed by the following complicated equation:

$$\ln S_1^\infty = \ln\left(\frac{T_{STP}}{P_{STP}T}\right) + r_1^0\left\{\left[1 + \left(\frac{v_1^*}{v_2^*} - 1\right)\frac{\rho_2^*}{\rho_2^0}\right]\right.$$
$$\left.\times \ln\left(1 - \frac{\rho_2^0}{\rho_2^*}\right) + \left(\frac{v_1^*}{v_2^*} - 1\right) + \frac{\rho_2^0}{\rho_2^*}\frac{T_1^*}{T}\frac{2\Psi\sqrt{P_1^*P_2^*}}{P_1^*}\right\} \qquad (24)$$

where superscript STP indicates standard temperature and pressure conditions; v_1^* and v_2^* are volumes occupied by a mole of lattice site of pure substance; $r_1^0 = M_1/(\rho_1^*v_1^*)$ and means the number of lattice sites occupied by solute molecules in its pure phase; and Ψ is the only adjustable parameter. When sufficient experimental data of infinite dilution solubility coefficients are available for different solutes, it is possible to retrieve the characteristic parameters for the polymer.[98] Thus, this model can be relatively easily applied to treatment of infinite dilution solubility coefficients of solutes in polymers and their temperature dependencies.

Inverse Gas Chromatography as a Probe Method. The probe methods are known as approaches for estimation of the sizes of free volume elements in polymers.[99] An examination of Table 2 shows that in PVTMS for the solutes with molecules larger than C_6−C_7 the dependence of $\overline{h}_1^{E,\infty}$ versus the critical volume V_c of the solute stops to be decreasing and $\overline{h}_1^{E,\infty}$ rapidly approaches the values characteristic for polymers above T_g. It was assumed[51] that it was related to inability of the solutes of larger size to accommodate the free volume elements in this polymer.

Further studies of the polymers with widely varying gas permeability confirmed the conclusions made for PVTMS that the coordinate of the minimum of the dependence of $\overline{h}_1^{E,\infty}$ on V_c can characterize the average size of free volume elements. In many cases, these minima were observed,[52,53,100] and the coordinate of the minimum ($V_{c,min}$) correlated with the permeability of the polymer. In addition, it was shown that the free volume element size determined as described above is in agreement with the data of the positron annihilation lifetime method.[99] The agreement of the sizes of the free volume element estimated by means of different probe methods[99] shows that the density of vapor molecules accommodated in free volume elements of glassy polymers is close to the density at the critical point. A comparison of IGC data with the results of other probe methods for the Hyflon AD80 copolymer[101] showed that this technique is applicable to estimation of the free volume element size. The molecular dynamics simulation of polymers indicated that high permeability polymers (such as PTMSP, amorphous Teflon AF2400, and PIM-1) have a broad size distribution of free

volume elements.[102,103] Therefore, one should expect a less deep minima in the correlation between $\overline{h}_1^{E,\infty}$ and V_c.

Solubility Coefficients in Rubbery and Glassy States. One more important difference between rubbers and high free volume glassy polymers is the enhanced values of the solubility coefficients in glassy polymers. Table 5 illustrates this point using two rubbers and a glassy polymer as examples.

Table 5. Solubility Coefficients S (cm^3 (STP)/cm^3 atm) of n-Alkanes in Glassy Additive PTMSN and Two Rubbers at Room Temperature Estimated by the IGC Method

solute	additive PTMSN[53]	PPM[49]	NR[27]
C_3H_8	80	5.0	6.3
n-C_4H_{10}	300	20	
n-C_5H_{12}	600	50	62
n-C_6H_{14}	2500	140	
n-C_7H_{16}	10000	370	
n-C_8H_{18}	20000	900	

Many other examples of such behavior can be found in the literature, including those provided by membrane studies.[104] It is evident from this table that highly permeable glassy polymer exhibit much greater solubility coefficients than rubbers. The cause of this feature lies in the fact that high permeability polymers have a large fraction of the nonequilibrium free volume, which is expressed also in high Langmuir sorption capacity C_H' of the empirical dual-mode sorption model.[105,106]

4. SORPTION ISOTHERMS AND SOLUBILITY COEFFICIENTS

Sorption isotherms, that is, the dependencies of the concentration of dissolved compound c on its vapor pressure p or activity in vapor phases p/p_s, where p_s is the saturated vapor pressure, are a key characteristics of the system polymer−gas (vapor). They are important for diverse technical applications and, in particular, for description of gas or vapor transport in polymers. Numerous methods for estimation of sorption isotherms (in particular, gravimetric and volumetric) are known (see for example reviews[107,108]). Obtaining a sorption isotherm is usually a time- and effort-consuming experimental task, so a dynamic determination of sorption isotherms by means of IGC seems to be an attractive option due to its express character.

The initial slope of the sorption isotherms $c(p)$, i.e., c/p at $p \rightarrow 0$, is the solubility coefficient S. In gas separation membrane studies the S value is estimated as the ratio P/D, where P is the permeability coefficient and D is the diffusion coefficient. A peculiarity, but also a limitation, of IGC as compared to standard, static thermodynamic methods is a possibility to work at low activity (low partial pressure) or small fraction of the sorbed component. As a rule, the quantity of the introduced solute in the IGC experiments is extremely small and well corresponds to the conditions of infinite dilution according to the solute. In these conditions any isotherm can be approximated by the linear Henry isotherm. In terms of chromatographic experiment it means independence of the retention time and volume on the size of introduced sample. The literature provides numerous confirmations of such behavior.[46,56,66,109] For larger samples when deviations from linear isotherms become significant, it can be recommended to make extrapolation to zero size of the sample.[4,110,111] As it has been shown,[4] the V_g values extrapolated to zero coincide for the chromatographic columns with different

content of polymer phase. On the other hand, using the dependence of the retention time on the size of the sample, it is possible to estimate the distribution constants as a function of the sample's size and construct the sorption isotherms.

Thus, the first and the simplest approach for the determination of the sorption isotherm is a chromatographic determination of the solubility coefficient S at infinite dilution (i.e., the initial slope of the isotherm), so Henry's type of isotherm $c = Sp$ can be obtained. This procedure is rather common in sorption of organic vapors. Often it is desirable to have sorption isotherms of light gases what is hardly possible using IGC. On the other hand, this limitation is not so important because of fulfillment of general correlations of the solubility coefficients with squared critical temperature T_c^2 or with the ratio $(T_c/T)^2$. These correlations hold for both vapors and gases[100,112] (see in more detail later).

The next step in obtaining the isotherms in a wider range of vapor activity is conducting the IGC experiments at finite concentrations of the solutes. In such works instead of using helium as a carrier gas, it is recommended to use mixtures of helium with the gas to be studied. So the chromatographic peak of a gas introduced into the column is obtained on the background of a finite (sometimes large) concentration of the same gas in the gas phase. In such a way it is possible to determine the activity coefficients and other thermodynamic parameters at finite solute concentrations.[113−117] However, this technique is rather troublesome. While using it, all the advantages of the express IGC method disappear. Though, the work with finite concentrations of solutes was successfully employed for investigation of cluster formation and microstructure of polymers.[118] In particular, this approach allowed these authors to study nonrandom partitioning of solute molecules and spatial correlation of polymer chains in a bulk.

It is known[2,6,10] that there exists direct relationship between the shape of chromatographic peaks and the form of sorption isotherm as is illustrated in Figure 9. In the case of Henry's law isotherm a symmetrical (Gaussian) peak is observed. In glassy polymers that are characterized by isotherms concave to the pressure axis and described by the dual-mode sorption model, a
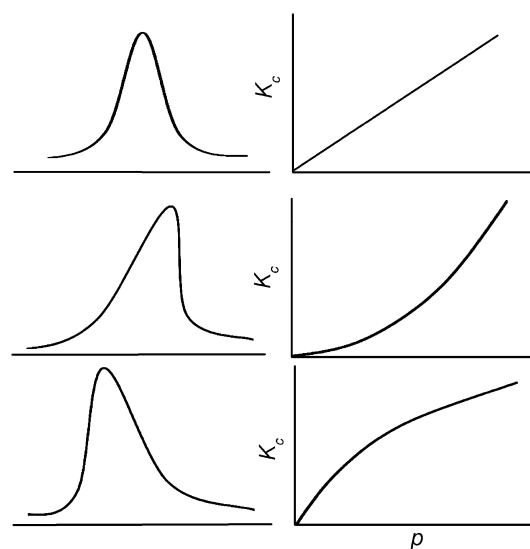
Figure 9. Shapes of chromatographic peaks and the form of sorption isotherms. From top to bottom: Henry isotherm, Flory−Huggins isotherm, and dual-mode sorption isotherm.

skewed peak with elongated "tail" is observed. On the other hand, sorption in rubbers with isotherms convex to the pressure axis and described by the Flory−Huggins model leads to peaks with elongated "entering edge".

So from the shape of chromatographic peak one can immediately recognize the form of sorption isotherm and the physical state (glassy or rubbery) of the polymer phase in the column. However, it is a much more complicated task to find the parameters of the sorption isotherm on the basis of experimentally observed peak. Meanwhile, the construction of sorption isotherms based on an analysis of the shape of a single peak remains an attractive problem. The ideas of such an approach have been formulated and experimentally studied in classical works by DeVault,[119] Gluekauf,[120] and Kiselev and Yashin.[1,2] First, this method was mainly applied for obtaining adsorption isotherms on inorganic sorbents. Gray and Guillet[109] used it for evaluation of the initial slope of the adsorption isotherm of n-decane on PMMA at the temperatures below the glass transition temperature of this polymer. However, Kiselev in refs 1 and 2 and elsewhere emphasized that IGC is a dynamic method, so sometimes the sorption isotherms obtained using this method can differ from equilibrium isotherms obtained by traditional (static) methods.

Some advantages are characteristic for another version of the IGC technique, namely for elution of the injected solvent on a concentration plateau of the same solvent in a carrier gas (e.g., nitrogen). It is called sometimes the elution-on-a-plateau method.[113,114] The theory of this method was formulated in a series of works by Conder and Purnell.[31,121,122] They demonstrated applicability of this experimental approach first in the case of gas−liquid chromatography (the system of n-hexane/squalane and n-heptane/dinonyl phthalate at solute's activities up to 0.7).[122] Later the same method was used[123,124] for polymer systems and resulted in obtaining the sorption isotherms in the systems n-hexane/high density polyethylene and aromatic solutes in polystyrene.

An original method for IGC investigation of sorption thermodynamics was proposed by Kotelnikova and Ageev.[125,126] These authors worked with solutes (water, alcohols) that were characterized by significantly asymmetric peaks, and the aim was to elucidate interactions with specific sorption sites in polymers. They used relatively large solute's samples. The treatment of the experimental data allowed them to obtain retention volumes that corresponded to certain concentrations of solutes in vapor phase and in polymers. The polymers studied in ref 125 were PVTMS, sulfonate-containing polyamides, polyelectrolyte complexes of chitozan, and poly-(acrylic acid). The isotherms obtained in glassy PVTMS at relatively wide range of activity p/p_s are convex to the concentration axis, in agreement with expectation of the dual-mode sorption model;[108] however, no comparisons were made with the data of static sorption.

Strongly asymmetric peaks were observed in sorption of water vapor in cellulose and its esters.[69] The resulting isotherms were obtained in the range of activity p/p_s = 0.03−0.5. They were also convex to the concentration axis, in agreement with the dual-mode sorption in glassy polymers[108] and were in a reasonable agreement with the results of static sorption measurement.

If the model of sorption isotherm is known, e.g. Flory−Huggins model for polymers above their glass transition temperature, so using a single parameter χ_{12}^{∞} estimated at infinite dilution (provided it is independent of the composition of the system), it is possible to find the sorption isotherm. Isotherms

obtained in this manner are presented for example in Figure 10.[127]
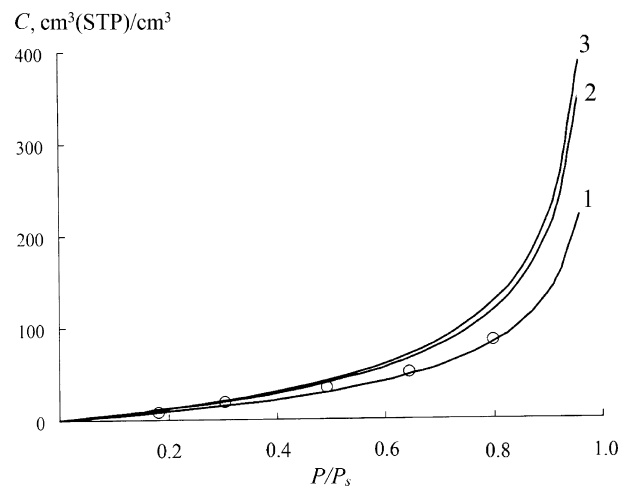
Figure 10. Sorption isotherms of n-hexane in rubbery (1) poly-(dimethylsilmethylene), (2) poly(dimethylsiltrimethylene) and (3) copolymer of dimethylsilmethylene and dimethylsiltrimethylene (34/66) at 40 °C. The data points correspond to the experimental values.[127]

In conclusion, measurement of bulk sorption isotherms in rubbers (or in polymers above their T_g) is now a common and quite applicable task. A more difficult but still attractive is the problem to obtain absorption isotherms in glassy polymers. Still, some attempts to realize this task have been made.[57,125,126]

As has been noted in section 2 of this Perspective, Kawakami and Kagawa[27] proposed the formula for calculation of the solubility coefficients S via the specific retention volumes V_g. They reported the solubility coefficients for several hydrocarbons in natural rubber. An assumption was made[29] that it is necessary to introduce a correction for nonideal behavior of vapor phase, so eq 4 becomes

$$S^{\infty} = \frac{1}{p^0} \rho_L V_g \exp\left(\frac{2B_{13} - V_1^{\infty}}{RT} p_1^0 j_3^4\right) \tag{25}$$

where B_{13} is the second mixed virial coefficient between solute gas and carrier gas, V_1^{∞} is the partial molar volume of solute in infinite dilution, and the term j_3^4 is the standard correction for pressure drop in the column. However, it was shown[27] that the introduction of this correction only marginally changes the obtained S values (the correcting coefficient is in the range 1.0008−1.0038), so usually this correction is neglected. In this work the chromatographic method allowed the authors[27] to determine the solubility coefficients of a number of solutes (hydrocarbons C_2−C_5) in natural rubber. A detailed comparison was made with the results of traditional methods of determination of S.[128,129] Subsequently, the solubility coefficients of gases and vapors estimated via the IGC method were extensively reported and discussed in the literature (see e.g. refs 49, 66, and 130−134).

As has been mentioned, the specific retention volumes V_g are virtually solubility coefficients S expressed in unusual units. The solubility coefficients in standard units can be found if the density of polymers ρ is known. The literature on IGC includes numerous V_g values obtained at different temperatures and for diverse solutes. In particular, a big compilation of the specific retention volumes (or solubility coefficients) is reported[61] for 9

polymers and 39 solutes at different temperatures. Table 6 gives as an example the solubility coefficients extrapolated[56] to the ambient temperature in the two polymers studied in different works.

Table 6. Solubility Coefficients (cm³ (STP)/cm³ atm) of Gases and Vapors at 25 °C

solute	polypropylene[a]	polydimethylsiloxane[b]
propane	6.5	8.6
n-butane	16.2	27.0
n-hexane	99.5	209
n-nonane	1310	3835
cyclohexane	202	379
benzene	157	354
CH_2Cl_2	39.0	86.4
$CHCl_3$	90.0	209
ethanol	11.8	40
n-propanol	30.8	12.6

[a]The data were taken from several works reported V_g at different temperatures.[61,135−139] [b]The data were taken from several works reported V_g at different temperatures.[62,113,133,140−146]

It is important to be sure that the found values of V_g are in agreement with the S values found using gravimetric measurements or as the ratio P/D. It is worth to remember that in the IGC experiments the polymer under investigation is studied as a thin film coated onto the surface of solid carrier or capillary column. The thermodynamic properties of such films and bulk polymer can differ.[147] Nevertheless, the IGC data successfully stand such tests. Some examples of such comparison for the solubility coefficients are given in Tables 7 and 8.

Table 7. Solubility Coefficients S (cm³ (STP)/cm³ atm) at 25 °C in Two Rubbers

| gas	IGC	volumetric method	P/D
	polydimethylsiloxane		
C_3H_8	8.35,[61] 8.2[66]	8.5[148]	
n-C_4H_{10}	26.8[61]	25[149]	
	natural rubber		
C_3H_8	5.7,[66] 6.3[27]		6.3[66]
n-C_4H_{10}	19.8[66]		19.5[66]

Table 8. Solubility Coefficients S (cm³ (STP)/cm³ atm) at 25 °C in Glassy PVTMS

gas	IGC[66]	gravimetric method[150]	P/D[66]
C_2H_4	3.6	3.6	3.4
C_2H_6	7.2	5.3	4.4
C_3H_6	23.0	33.5	37.0
C_3H_8	27	30.4	

It is seen that for both rubbery and glassy polymers a reasonable agreement between the S values found via IGC and independent (traditional) methods is reached. Similar tests have been undertaken for other thermodynamic parameters found by IGC (for example, for the activity coefficients[145]), and as a rule they revealed a good agreement.

It is well-known that for the solubility coefficients of light gases in polymers good linear correlations hold with such parameters as critical temperature T_c, boiling point T_b, and Lennard-Jones energy parameter ε/k.[151] The IGC values also obey those

correlations as was demonstrated already in ref 27. Meanwhile, joint consideration of the data for light gases (traditional determination of S) and the data for vapors (IGC method) allows a significant expansion of the range of these correlations. Thus, for the standard set of gases (He, H_2, O_2, N_2, CO_2, CH_4) the critical temperature T_c varies from 4 to 304 K. On the other hand, inclusion of the data for e.g. alkanes $C_4–C_{13}$ that can easily be studied using IGC expands the upper bound of this range of T_c up to 650 K.[100] More important, new regularities appear in this case. Thus, for amorphous Teflon AF2400[100] as well as for several other glassy and rubbery polymers,[49,53,54,130] it was shown that linear correlation with T_c for the solubility coefficients is replaced by the linear correlation with T_c^2 or with $(T_c/T)^2$. An example of such correlation is shown in Figure 11.
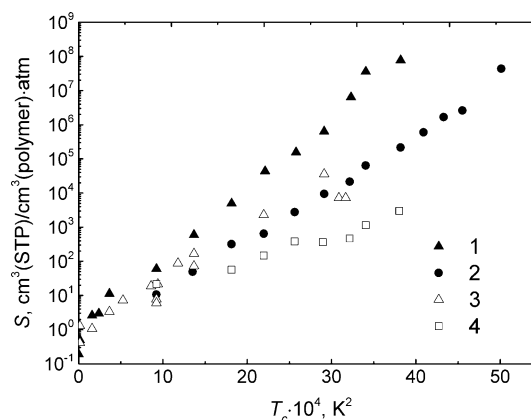
Figure 11. Correlation of the solubility coefficients of gases and vapors with T_c^2 in different polymers: (1) polymer of intrinsic microporosity PIM-1,[54] (2) additive poly(trimethylsilylnorbornene),[53] (3) poly-(trimethylsilylpropyne),[152] (4) PVTMS.[51] Reproduced from ref 153.

It is caused by rapid increases in the enthalpy of condensation ΔH_c for heavier vapors, which explains faster growth of S values for such solutes.[100] It should be noted that such correlations of the solubility coefficients have been independently noted using the S values obtained via traditional methods.[105] Besides, Stiel and Harnish[154] obtained a similar correlation based on the IGC study of 16 organic solutes in molten polystyrene at 135−225 °C.

In Figure 11, a part of the data, namely the S values for light gases (i.e., the data points at lower T_c), were not obtained via IGC. Meanwhile, a very good agreement is observed between these data and the S values for heavier solutes, since all the points are located along the same line. It means that the IGC method can be useful also for indirect assessment of the solubility coefficients for light gases.

The correlations of V_g or S with T_c or T_b are fulfilled for polymer−solute systems where only van der Waals interactions take place. Appearance of hydrogen bonding can change the situation significantly. Thus, sorption of chloromethanes (CCl_4, $CHCl_3$, and CH_2Cl_2) in copolymers of chloroprene and methyl methacrylate and methacrylic acid the two latter solutes can exhibit hydrogen bonding with the copolymer. Hence, thanks to this, the order of the V_g or S values does not follow the changes of T_c of the solutes.[155,156] Chloroform having lower T_c had greater solubility coefficients than carbon tetrachloride. This observation was confirmed by FTIR results.[156]

Another thermodynamic parameter that has been measured in numerous IGC works is the sorption enthalpy ΔH_S defined by eq 5 as the slope of the dependence of ln V_g versus reciprocal

temperature. This equation would be very similar to the common definition of the enthalpy of gas sorption in polymers

$$\Delta H'_S = -R \frac{d \ln S}{d(1/T)} \tag{26}$$

but the temperature dependence of polymer density must be taken into account (see eq 4). However, the correction accounting for this factor is not large. According to van Krevelen[151] above the glass transitions the thermal expansion coefficient $\alpha_r = 6.3 \times 10^{-4} \, K^{-1}$, while for the glassy state it is $\alpha_g = 2.9 \times 10^{-4} \, K^{-1}$. More accurate data can be found in the handbook on PVT data[157] for the specific polymers. Thus, for polystyrene $\alpha_g = 2.0 \times 10^{-4} \, K^{-1}$ and $\alpha_r = 6.0 \times 10^{-4} \, K^{-1}$. This corresponds to the correction in ΔH_S in the glassy state of 0.16 kJ/mol and in the rubbery state of 0.5 kJ/mol. Both corrections are small in comparison with the estimated ΔH_S values. Thus, the literature on IGC contains numerous data on enthalpy of vapor sorption in polymers (see for example refs 61 and 158−161) that allows estimation of the solubility coefficients in a wide range of temperature. As a rule, this is not simple using traditional thermodynamic methods. Enthalpies of sorption ΔH_S of hydrocarbons in glassy and rubbery polymers are presented and discussed in Table 1.

5. DETERMINATION OF DIFFUSION COEFFICIENTS

As it follows from other sections of this Perspective, the IGC method is directed mainly to the determination of the thermodynamic properties of polymers and investigation of the interactions of polymers and low molecular mass compounds. However, IGC carries information not only on thermodynamics but also on diffusion properties of polymers. This seems to be especially attractive for those who use the IGC method in relation to the problems of membrane separation of gases and vapors. Indeed, the main parameter of membrane gas separation, the permeability coefficient P, can be presented as the product $S \cdot D$, where S is the solubility coefficient, while D is the diffusion coefficient, so the estimation of the both parameters using the same method is quite desirable. There are many important practical problems where the rate of diffusion of low molecular mass compounds (plasticizers, stabilizers, residual solvents or monomers, etc.) in polymers must be known at elevated temperatures. And here the use of IGC can be very helpful because the classical methods for determination of the D values are not always convenient.

In contrast to the determination of the S values, it is the width of the peak that can serve as a measure of the diffusion coefficient. If an infinitely narrow peak of a solute is injected into the column, then the widening of the peak is caused mainly by the diffusion of the solute within the polymer phase. Usually the width of the peak is characterized by the value "height of equivalent theoretical plate" or HETP (H). It is defined[3] as follows:

$$H = \frac{l}{5.54}\left(\frac{w_{hi}}{t_{Ri}}\right)^2 \tag{27}$$

where l is the column length, w_{hi} is the measured peak width at half the maximum height, and t_{Ri} is the retention time for the eluted compound. HETP is a measure of peak's efficiency in analytical gas chromatography: insufficiently narrow peaks would overlap, which is undesirable for analytical applications of chromatography.

The first successful application of the chromatographic method for determination of the diffusion coefficient was

proposed by Van Deempter et al.,[162] who studied classical gas−liquid chromatography in packed column (i.e., before appearance of IGC of polymers). They proposed the following formula for HETP as a function of the linear carrier gas flow rate u:

$$H = A + B/u + Cu \tag{28}$$

where A, B, and C are constants (they do not depend on u). Parameter A characterizes instrument widening of the peak, while B is related to widening due to the diffusion in gas phase. At small u the first two terms govern, and H is described as a hyperbole. At large u the function passes through a minimum and the experimental points approach the asymptote with the slope C that can be described as

$$C = \frac{8}{\pi^2} \frac{d^2}{D} \frac{k}{(1+k)^2} \tag{29}$$

where d is the thickness of the layer of polymer phases (average thickness in the case of packed columns), D is the diffusion coefficient of the solute in the polymer, and the parameter k is defined as the ratio $(t_r - t_a)/t_a$, where t_r and t_a are the retention times of the solute and the component (air or methane) which has negligible solubility in the polymer stationary phase. Figure 12 illustrates such plots of H.
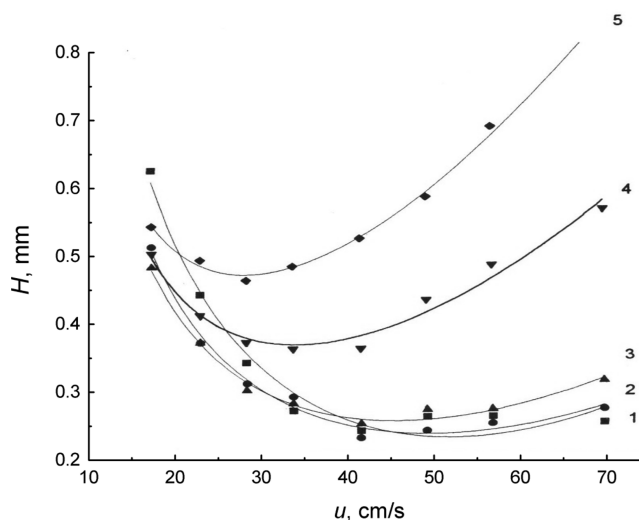
Figure 12. Dependence of H on the linear velocity of carrier gas in the column with PTMSP:[163] (1) CH_4, (2) C_2H_4, (3) C_2H_6, (4) C_3H_6, and (5) C_3H_8. Adopted from ref 156.

In spite of the principal possibilities opened by this method for the determination of the diffusion coefficients, its application implies certain difficulties. First, numerous measurements at different u are necessary to obtain a single value of D. Depending of particular values of the parameters of eq 28, the $H(u)$ curves reach the asymptote rather slowly, so an extended range of the u values is needed. However, many examples of the application of this method can be found in the literature.[139,164−174] The stationary phase coated onto solid supports in the packed columns can have a distribution of the thickness d, so the obtained D values are also distributed. These limitations disappear in the case of capillary columns, so namely for capillary columns the most accurate determinations of D were performed. Attempts to coat polymers over the surface of glass beads were not very successful.[167,161]

Table 9. Some of the Studied Systems Polymer−Solute[a]

polymer	T (°C)	diffusants	refs
polystyrene	110−180	C_6H_6, $C_6H_5CH_3$, $C_6H_5C_2H_5$, $n\text{-}C_6H_{14}$, $n\text{-}C_{10}H_{22}$	170, 199, 190, 191, 193[b]
PVAc	30−150	C_6H_6, $C_6H_5CH_3$, $C_6H_5C_2H_5$, C_6H_{12}, n-alkanes C_6−C_9, isoalkanes, olefins, dienes, MeOH, EtOH, methyl acetate, H_2O	170, 188, 189, 191,[b] 182,[b] 183, 200
poly(vinyl alcohol)	90−140	MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, methyl acetate, H_2O	172, 174, 200
PMMA	105−175	Me-Et, Pr-acetates	188
polydimethylsiloxane	150−200	n-alkanes C_5−C_{10}	173, 201
polyolefins			
PE	60−100	$n\text{-}C_5H_{12}$, $i\text{-}C_5H_{12}$, $n\text{-}C_6H_{14}$, 1-hexene, 1-octene	202
PP	100−120		139
PIB	50−100	$n\text{-}C_6H_{14}$, $n\text{-}C_7H_{16}$, $n\text{-}C_{10}H_{22}$	184, 197[b]
EPDM	50−200	Me_2CO, C_6H_6, $CHCl_3$, C_6H_{12}, MEK, $n\text{-}C_6H_{14}$, C_6H_{12}, dicyclopentadiene	192[b]
polyepichlorohydrin	35−65	$C_6H_5CH_3$	167
polysulfone	200−270	NMP, γ-butyrolactone, DMSO, THF, H_2O, CH_3COOH	194
poly(ether imide)	200−270	NMP, γ-butyrolactone, DMSO, THF, H_2O, CH_3COOH	194
copoly(methyl methacrylate−butyl methacrylate)	150−200	MeOH, EtOH, 1-PrOH, 1-BuOH, acetates, CH_2Cl_2, $CHCl_3$, acetone	198
copoly(styrene−acrylonitrile)	130−170	$n\text{-}C_5H_{12}$, $n\text{-}C_6H_{14}$, C_6H_{12}, C_6H_6, $C_6H_5CH_3$, xylenes	203
PTMSP[c]	31−120	C_2H_4, C_2H_6, C_3H_6, C_3H_8, $i\text{-}C_4H_{10}$, $n\text{-}C_4H_{10}$, 1-hexene, $n\text{-}C_6H_{14}$, $C_6H_5CH_3$	163

[a]In most cases the diffusion coefficients were measured above T_g and in the conditions of infinite dilution. [b]The works where D values were measured in the finite concentrations. [c]This polymer was studied in glassy state.

The approach proposed by Van Deemter et al.[162] obtained further development in the works by Giddings,[175] Galin,[176] and others. In particular, it was proposed[167,170,177] to use a more general expression

$$C = q \frac{d^2}{D} \frac{k}{(1 + k)^2} \tag{30}$$

that includes an adjustable parameter q, which can be estimated via independent data for the same diffusant−polymer systems obtained, e.g., in gravimetric experiments.

Another formula that was extensively used in the studies performed with capillary columns was proposed in the works by Giddings and Goley:[175,178−180]

$$H = B/u + C_m u \tag{31}$$

where B is the diffusion coefficient of the solute in gas phase and C_m is the total mass transfer resistance coefficient that can be presented as a sum $C_m = C_g + C_s$, where C_g and C_s are resistance coefficients in gas phase and condensed (polymer) phase, respectively. This equation was used in particular by Berezkin et al.,[163] who studied diffusion of various hydrocarbons in glassy PTMSP—a rare case when the IGC method was employed at the temperatures below the glass transition temperature of the polymer. In order to separate the effects of C_g and C_s on H, the authors studied the chromatographic process in the presence of two different carrier gas (He and CO_2) in the same capillary column. Using the so-called method of the reference point,[181] the authors could estimated the C_s values and via them the diffusion coefficients D. Many IGC studies of the diffusivity of polymers in open capillary columns were performed during the past decades.[182−185]

Another progress in this field was a creation of more sophisticated models that allow an estimation of the diffusion coefficients using analysis of the shape of a single chromatographic peak. Such models were proposed by Pawlish et al.[186,187] The models are based on the following assumptions: (1) instantaneous phase equilibrium at the polymer−gas interface; (2) isothermal conditions; (3) carrier gas is in steady state, laminar flow; (4) axial diffusion in the polymer film is negligible;

(5) the carrier gas is insoluble in the polymer; (6) surface adsorption is negligible; (7) the input pulse of the solute is a narrow and sharp spike.

With these assumptions the continuity equations for gas and polymer phases were written and after some treatment solved with Laplace transformation.[186] Otherwise, the Fourier transform algorithm was used with subsequent minimization of the deviations by using a nonlinear regression technique.[17,187] The resulting solutions include the diffusion coefficient in gas phase D_g, which is much larger than D_p, the diffusion coefficient in the polymer phase. Beside, the D_g values can be estimated independently using the known correlation. The diffusion coefficient D_p can be obtained from the dimensionless parameter β:

$$\beta^2 = \frac{\tau^2 u}{D_p L} \tag{32}$$

where τ is the thickness of polymer film (cm), u is the mean linear velocity of the carrier gas (cm/s), and L is the length of the column (cm). This model was checked using diffusivity of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) for over 30 different solutes at various temperetures.[188]

Subsequently, several variants of the models based on analysis of the shape of single chromatographic peaks (or its broadening due to diffusion) were considered.[182,189−195] These models were employed in numerous experimental studies.[184,196−198]

An advantage of IGC is a possibility to measure D in a wide range of values. The reported D values are in the range of from 10^{-5} to 10^{-13} cm^2 s^{-1}.

The diffusion coefficients were determined by means of the chromatographic technique for the polymers of various chemical structures, amorphous and semicrystalline, homopolymers and copolymers. Table 9 demonstrates a versatility of the studied systems. In many cases the solute studied was toluene, a convenient compound for testing the diffusivity of polymers measured by IGC and static methods. In some cases the choice of compounds in measurements were dictated by practical issues. For example, the compounds studied in ref 194 (N-methylpyrrolidone, etc.) served as solvents in formation of gas

separation membranes. Sometimes, it is important to check the presence of residual monomers in polymers, and in such cases the IGC method is suitable.[196] Measurements of the diffusion coefficients of alcohols by IGC are useful in relation to the pervaporation process.[172]

The classical and traditional IGC experiments are conducted in the conditions of infinite dilutions. In many cases it is of interest to measure the diffusion coefficients at larger (finite) concentrations of solutes. In particular, it is important for comparison with the results of static works on diffusivity that are performed namely at finite concentrations. The corresponding techniques have been developed and used in several works[17,182,191−193,197,200] for polymers of various structures. In such experiments, a reservoir filled with the solute is added to the standard gas chromatographic setup. The carrier gas is saturated with the solute at certain pressure. The polymer phase in the column is brought into equilibrium with such binary carrier gas. Then a small pulse of the same solute is injected into carrier gas and the resulting peak is analyzed in the same manner as in the case of infinite dilution. Injection of other solute is also possible, so interference of different solutes can be studied.

It was necessary to check novel chromatographic methods by comparison with static determination of D in traditional sorption experiments and with predictions of the free volume models for diffusivity. As a rule, such comparisons showed good agreement. Thus, it was demonstrated for the system PVAc−toluene,[191] polystyrene−hydrocarbons,[193] and polydimethylsiloxane−n-pentane.[201] Recently, a detailed study[200] showed that diffusivity of several solutes in PVAc and fully and partially hydrolyzed poly(vinyl alcohol) measured by capillary column inverse gas chromatography is in good consistency in terms of their temperature and concentration dependences with the results of gravimetric sorption measurements.

6. CONCLUDING REMARKS

Today the inverse gas chromatography is established as an efficient method of physical chemistry of polymers. Several hundred papers have been published on IGC, and they provide information on various interactions as discussed in the Introduction. However, in some respects the data accumulated in numerous IGC investigations are underestimated today. Just as the Daynes−Barrer method in membrane science permits one in a single experiment to determine the permeability coefficient P, diffusion coefficient D, and indirectly solubility coefficient $S = P/D$, in the same manner IGC can give information on the distribution coefficients or S, on diffusivity D, and, hence, indirectly on P. Besides, the IGC method can give such information in the conditions quite difficult for the investigations in static conditions, i.e., at higher temperatures. Temperature dependences of these parameters are obtained rather easily by IGC, which cannot be said sometimes in the case of the static measurements. The list of low molecular mass compounds whose interactions with polymers have been studied is very long, and their properties such as critical temperatures vary in a wide range. All this implies that the literature of IGC keeps information potentially important for theory but also for different branches of applied polymer science (polymer processing, membrane separation, etc.). The thickness of polymer films in packed and capillary chromatographic columns is of the same order as the thickness of selective layers in composite membranes. So it can be assumed that the data obtained in the IGC experiments are applicable for description of such membranes, an additional argument for joint consideration of IGC and membrane data.

An important direction that requires further development is the determination of the sorption isotherms using IGC. Potential objects of such studies are both rubbery and glassy polymers, especially high free volume glassy materials.

Meanwhile, IGC has an important disadvantage: it does not allow one to estimate the interactions of polymers with light gases. A development of corresponding procedure will be a great stride that would significantly expand applications of IGC.

In our opinion little attention has been paid to thermodynamic properties of glassy polymers. Of course, diffusion limitations preclude investigation of glassy polymers except a small group of polymers with extra large free volume. However, diminishing of the thickness of the coated films may partly overcome this problem. It will be desirable to focus more attention on sorption behavior of solutes in polymeric materials in the vicinity of their glass transition temperature. Such works may give an impact to better understanding of polymer solution thermodynamics in glassy state.

An interesting problem for future IGC studies is an elucidation of unusual behavior of perfluorinated and partly fluorinated polymers—materials that do not obey Hildebrand's regular solution theory—the problem that has not found so far its solution in spite of numerous studies.[204,205]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

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    Nomenclature (PDF)

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Notes
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