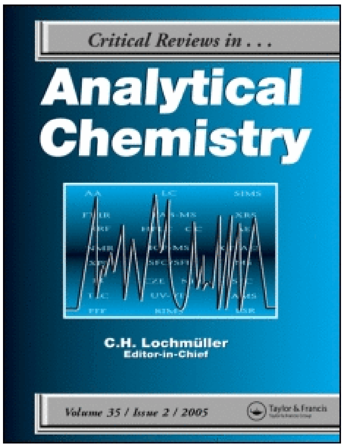

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Inverse Gas Chromatography: Characterization of Polymers, Fibers, Modified Silicas, and Surfactants

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Inverse Gas Chromatography: Characterization of Polymers, Fibers, Modified Silicas, and Surfactants

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ABSTRACT: Inverse gas chromatography is presented as a method of characterization of polymers, fibers, silicas, surfactants, and other materials. Theoretical background, parameters used for description of material's properties, data reduction process, preparation of columns, as well as reported results from 145 references are reviewed and discussed.

KEY WORDS: inverse gas chromatography, solubility parameters, polarity parameters, Flory-Huggins interaction parameter, polymer-polymer interaction parameter, acceptor-donor interactions, characterization of polymers, fibers, surfactants, silicas.

I. INTRODUCTION

During the years of evolution of gas chromatographic techniques, inverse gas chromatography (IGC) has become an accurate, reliable, and fast method for the physicochemical characterization of polymers and their blends,[1-28] fibers,[29-30] modified silicas and other surfaces[31-41] and surfactants,[42-51] as well as commercial stationary phases and their mixtures,[52] petroleum pitches,[53,54] and heavy residues of oil distillation.[55] This technique also has been used to study the water sorption ability of different materials.[56-57] The term *inverse* indicates that the examined material (e.g., a polymer blend or a modified silica) is placed in a chromatographic column and studied using test solutes, in contrast to the typical use of analytical gas chromatography. Carefully selected testing solutes are injected into the flow of a carrier gas and transported over the surface of a material such as fiber. The retention time and peak elution profiles of standard solutes, influenced by interactions between the solute and stationary phase, are used to estimate their interactions. Actually, we should separate inverse gas chromatography into inverse gas-liquid chromatography and inverse gas-solid chromatography. It is obvious that the basis of this discrimination is the state of the column contents being examined. Polymers, commercial stationary phases, or surfactants represent liquids that have been studied, under experimental conditions involving a mixed mechanism of retention of the test solutes. Modified silicas are examples of solids that have been studied, and, in this case, adsorption effects predominate, while solution partition in graft chains seems to be negligible. However, Vidal et al.[31] observed effects that could be attributed to solution effects in longer alkyl chains.

The basic IGC assumption is that solute equilibrium conditions are achieved between the mobile and stationary phases. Pawlisch et al.[9] conducted studies on polymers using small volumes of injected probes (<2 μl), that provided interactions in the gas chromatographic column that occur at concentrations approaching infinite dilution. The high sensitivity of using retention behavior for studies of the structure of polymers, surfactants, fiber surfaces, and adsorbents allows for broad applications of the IGC technique. Thermodynamic studies of solute interactions with

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different types of surfaces have been examined, and activity coefficients at infinite dilution (Ω^∞), the Flory-Huggins interaction parameter (χ_{12}), solubility parameters (δ_i), diffusion constants, enthalpies, entropies, partial molar free energies of mixing (ΔG^∞), and surface sorption characteristics—the standard free energy and enthalpy of adsorption, the surface energy of silica/modified silica, and its dispersive component, as well as donor-acceptor interactions, adsorption isotherms, the isosteric heat of adsorption, transition temperatures, the degree of crystallinity, the partial molar free energy of solution for the methylene group [$\Delta G^E(CH_2)$], the partial molal free energy, enthalpy and entropy of solution, polarity parameters, and others—were derived from the retention data. In polymer chemistry, interfacial interactions play an important role in determining the properties of materials. These interfacial forces range from strong covalent or ionic chemical bonds to weak van der Waals interactions. Very often interfacial properties are only determined by the nonbonded interactions. Fowkes[58] and Chen[16] suggested the possibility of estimating parameters for characterizing acceptor-donor interactions at the interface of polymers. Vidal et al. reported on the estimation of appropriate parameters for the surface of modified silicas.[31]

A measurement temperature of 40 to 50°C above the glass transition temperature of polymers, T_g, has been suggested for thermodynamic estimations.[15,19] However, experiments carried out below and above the glass transition temperature studying a blend of components,[8] or at the melting point of semi-crystalline polymers, have been reported.

Smidsrod and Guillet[60] found that the retention diagram of an amorphous polymer depends strongly on the test solute and could be divided into three isotherms: equilibrium surface adsorption, nonequilibrium surface adsorption, and equilibrium sorption. Semicrystalline polymers are characterized by an additional phase transition below their melting-point temperature.[60,61]

Characterization criteria are sorely needed that could help chromatographers compare a number of the offered commercial stationary phases in order to reduce their number and, ultimately, to be able to make appropriate selections according to their solvent strength and selectivity. Gas chromatographic stationary phases can be characterized in terms of their solvent strength (polarity). Poole and Poole[62] define this as the capacity of a solvent for various intermolecular interactions. Solvent selectivity, on the other hand, is the *relative* capacity of solvents for particular intermolecular interactions. The most popular stationary phases in gas chromatography are polymers of high molecular weight or their mixtures.[63-65] Surface-active agents of different types also have been examined as stationary phases in GC experiments.[42-51] A large number of papers on the characterization of GC stationary liquid phases have been published. Some of those deemed more important, including some review articles, are referred to herein.[62,66-70] The most significant conclusions from the work of Poole et al.[62] can be summarized as follows: (1) there is no single test solute that can be used to determine the polarity of a stationary phase; (2) the partial molal Gibbs free energy of solution for a methylene group seems to be the most appropriate parameter; (3) solvent selectivity is probably best characterized by differences in the partial molar (or molal) Gibbs free energy of solution for a series of test solutes on two phases (one being a nonpolar reference phase); and (4) particular attention should be paid to the influence of interfacial adsorption, both at the gas-support and gas-liquid interface.

Thermodynamic characterizations of polymers or their mixtures as liquid GC stationary phases have also been published.[2,4,61-79]

II. CHARACTERISTICS USED IN INVERSE GAS CHROMATOGRAPHY

A. Mixed Retention Mechanism

Present knowledge of the retention mechanism in gas-liquid chromatography distinguish at least three ways in which a test solute might interact with column packing: (1) partition between the gas and liquid phase (V_L), (2) adsorption at the gas-liquid interface (A_{GL}); and/or (3) adsorption at the liquid-solid interface (A_{LS}). The net retention volume V_N^* of a solute (per gram of column packing) can then be expressed as:

$$V_N^* = V_L K_L + K_{GL} A_{GL} + K_{LS} A_{LS} \qquad (1)$$

where K_L is the partition coefficient, K_{GL} is the adsorption coefficient at the gas-liquid interface, and K_{LS} is the adsorption coefficient at the liquid solid interface.[62]

However, Equation 1 is only valid if any contribution from the structured liquid-phase layer can be neglected. This depends on the properties of the support and the column temperature. Poole et al.[62] stated that Equation 1 is generally true at phase loadings exceeding 10% (w/w) (i.e., the bulk liquid case). Adsorption at the support surface could also contribute to retention. Careful deactivation of the support surface and the use of higher liquid loadings can minimize this undesirable effect. The resistance to mass transfer in highly viscous polymers could be an impediment to the attainment of equilibrium conditions.

Poole et al.[62] have used K_L estimated from a rearranged version of Equation 1 to calculate both polarity and selectivity parameters of stationary phases. They redefined the well-known Kovats' equation, which is used to calculate retention indices that describe only the partitioning of an analyte between the stationary phase and the carrier gas.

B. Flory-Huggins Interaction Parameter and Thermodynamic Parameters

The Flory-Huggins solute-polymer interaction parameter $\delta_{1,2}^{\infty}$ may be given as:

$$\varkappa_{1,2}^{\infty} = \ln\left(\frac{273.15R}{P_1^{\circ} V_g^{\circ} M_1}\right) - \frac{P_1^{\circ}}{RT}(B_{11} - V_1^{\circ}) + \ln\frac{\rho_1}{\rho_2} - \left(1 - \frac{V_1^{\circ}}{V_2^{\circ}}\right) \qquad (2)$$

where M_1, P_1°, B_{11}, V_1°, ρ_1, and V_g° are the polymer molecular weight, the saturated vapor pressure of the pure solute at column temperature T, the second virial coefficient, the molar volume, and the specific retention volume of the solute, respectively; ρ_2 and V_2° are the density and molar volume of the polymer at the temperature, respectively; T is the column temperature (°K); and R is the gas constant. Hence, this parameter is defined by the solute-specific retention volume and not by the partition coefficient K_L. Special attention is essential in the determination of retention data in order to obtain V_g° values that are free from solute adsorption effects at the gas-liquid, liquid-solid, and gas-solid interfaces. The procedures proposed by different investigators will be discussed in the following sections of this paper.

For the case of the mixture of two polymers, Equation 2 could be rearranged into[8,52]

$$\begin{aligned}\varkappa_{1,m}^{\infty} = {} & \ln\left(\frac{273.15R}{P_1^{\circ} V_g^{\circ} M_1}\right) - \frac{P_1^{\circ}}{RT}(B_{11} - V_1^{\circ}) \\ & + \ln\frac{\rho_1}{\rho_m} - \left(1 - \frac{V_1^{\circ}}{V_2^{\circ}}\right)\phi_2 \\ & + - \left(1 - \frac{V_1^{\circ}}{V_3^{\circ}}\right)\phi_3, \end{aligned} \qquad (3)$$

where, at column temperature T, ρ_m is the density of the mixture of the polymers, V_2° and V_3° are the molar volumes of the components of the polymer blend, and ϕ_2 and ϕ_3 are their volume fractions, respectively.

The free energy of mixing of a test solute with such an examined blend is then expressed by[8]

$$\begin{aligned}\Delta G_{mix} = {} & RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 \\ & + n_1\phi_2\varkappa_{12}^{\infty} + n_1\phi_3\varkappa_{13}^{\infty} + n_2\phi_3\varkappa_{23}^{\infty}] \end{aligned} \qquad (4)$$

where $\phi_{1\text{-}3}$ and $n_{1\text{-}3}$ are the volume fractions and mole numbers of the components of the interacting system and $\varkappa_{ij}^{\infty}$ values are binary interaction coefficients.

The polymer-polymer interaction parameter $\varkappa_{23}^{\infty}$ is usually related to the size of the probe molecule and is defined as[8,18,65]

$$\begin{aligned}\varkappa_{23}' & = \frac{\varkappa_{23}^{\infty} V_1^{\circ}}{V_2^{\circ}} \\ & = \frac{1}{\phi_2\phi_3}\left[\ln\frac{V_{g,m}^{\circ}}{W_2\nu_2 + W_3\nu_3} - \phi_2 \ln\frac{V_{g,2}^{\circ}}{\nu_2} - \phi_3 \ln\frac{V_{g,3}^{\circ}}{\nu_3}\right] \end{aligned} \qquad (5)$$

where ν_2, ν_3, and W_2, W_3 are the specific volumes and weight fractions of the components; $V^{\circ}_{g,2}$, $V^{\circ}_{g,3}$, and $V^{\circ}_{g,m}$ are the specific retention volumes of the test solute on the column with polymer 2, polymer 3, or their mixture, respectively.

Fernandez-Sanchez et al.[52] calculated $\varkappa'_{23}$ according to the equation:

$$\varkappa^{\infty}_{1(23)} = \varkappa^{\infty}_{1,2}\phi_2 + \varkappa^{\infty}_{1,3}\phi_3 - \varkappa'_{2,3}\phi_2\phi_3 \quad (6)$$

using the interaction parameters obtained previously on columns containing the mixture of polymers and each of the components separately.

The polymer-polymer interaction coefficient is employed to characterize the level of binary interactions between the two polymers. It is commonly related to the second virial coefficient B_{23} by

$$B_{23} = RT\varkappa'_{23}/V^{\circ}_1 \quad (7)$$

The weight fraction activity coefficient at infinity dilution is usually[1,3,10,11,13,14,17,52,72] calculated according to

$$\ln \Omega^{\infty}_1 = \ln\left(\frac{273.15R}{P^{\circ}_1 V^{\circ}_g M_1}\right) - \frac{P^{\circ}_1}{RT}(B_{11} - V^{\circ}_1) \quad (8)$$

The partial molar free energy (ΔG^{∞}_1) and enthalpy (ΔH^{∞}_1) of mixing at infinite dilution of the solute are given by

$$\Delta G^{\infty}_1 = RT \ln \Omega^{\infty}_1 \text{ and} \quad (9)$$

$$\Delta H^{\infty}_1 = R\,\frac{\delta(\ln \Omega^{\infty}_1)}{\delta(1/T)} \quad (10)$$

It is well known that the excess partial molar heat of mixing ΔH^{∞}_1 can be obtained from the relation

$$\Delta H^{\infty}_1 = \Delta H_v + \Delta H_s \quad (11)$$

where ΔH_v is the heat of vaporization from solution

$$\Delta H_v = R\,\frac{\delta(\ln V^{\circ}_g)}{\delta(1/T)} \quad (12)$$

and ΔH_s is the heat of solution

$$\Delta H_s = -R\,\frac{\delta(\ln V^{\circ}_g)}{\delta(1/T)} \quad (13)$$

The partial molar free energy of sorption (e.g., by the amorphous part of the polymer or polymer blend[17]) at infinite dilution is calculated from

$$\Delta G^{s}_1 = RT \ln \frac{M_1 V^{\circ}_g}{273.13R} \quad (14)$$

and the entropy of sorption from the basic Gibbs equation,

$$\Delta G^{s}_1 = \Delta H^{s}_1 - T\Delta S^{s}_1 \quad (15)$$

Edelman and Fradet[13] considered the possibility of the description of polymer systems by $\varkappa^{\infty}_{ES}$ according to Flory's equation-of-state theory[78-81] (ES theory):

$$\varkappa^{\infty}_{ES} = \ln \Omega^{\infty}_i + \ln(\nu^*_2/^*_1) - 1 + v^*_1/v^*_2 \quad (16)$$

where ν^*_1 and v^*_1 are characteristic volumes. They also discussed the $\varkappa^{\infty}_{LF}$ interaction parameter as derived from the lattice-fluid theory (LF) of Sanchez and Lacombe[70-72] and defined by an equation, similar to Equation 16, as

$$\varkappa^{\infty}_{LF} = \ln \Omega^{\infty}_1 + \ln\left(\frac{\rho^*_{1LF}}{\rho^*_{2LF}}\right) - 1 + \frac{V^*_{1LF}}{V^*_{2LF}} \quad (17)$$

where ρ^*_{iLF} and V^*_{iLF} are the characteristic densities and molar volumes.

However, they stated that the ES or the LF theories do not exhibit any significant advantages over the Flory-Huggins theory. All considered interaction parameters, i.e., $\varkappa^{\infty}_{12}$, δ^{∞}_{ES}, and $\varkappa^{\infty}_{LF}$, varied similarly with temperature.[13]

C. Solubility Parameters

The solubility parameter is defined as the square root of the cohesive energy density, defined as the ratio of the energy of vaporization to the molar volume:

$$\delta \equiv \left(\frac{\Delta E_v}{V_1^\circ}\right)^{1/2} \tag{18}$$

The solubility parameter of a substance at a given temperature may be calculated as follows:

$$\delta_1 = \left(\frac{\Delta H_v - RT}{V_1^\circ}\right)^{1/2} \tag{19}$$

where ΔH_v is the molar enthalpy of vaporization of substance (1) at temperature T and R is the gas constant.

Polymers have very low vapor pressures, and the direct calculation of δ_1 according to Equation 19 is not possible. Guillet et al[3,86] evaluated solubility parameters under the assumption that the interaction parameter χ^∞ has free energy characteristics with enthalpic (χ_H^∞) and entropic (χ_S^∞) terms:

$$\chi^\infty = \chi_H^\infty + \chi_S^\infty \tag{20}$$

As

$$\chi_H^\infty = \frac{V_1^\circ(\delta_1 - \delta_2)^2}{RT} \tag{21}$$

then

$$\chi^\infty = \frac{V_1^\circ(\delta_1 - \delta_2)^2}{RT} + \chi_s^\infty \tag{22}$$

This equation may be rewritten as

$$\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V_1^\circ} = \frac{2\delta_2}{RT}\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_1^\circ}\right) \tag{23}$$

Plotting the left-hand side of Equation 23 vs. δ_1, one obtains a straight-line slope proportional to δ_2 of the polymer.[3,52,85]

The difference between the solubility parameters of two mixture components is related by

$$\delta_1 - \delta_2 = \left(\frac{\Delta E_{vm}}{\phi_1\phi_2 V_m}\right)^{1/2} \tag{24}$$

where ΔE_{vm} is the energy of mixing of the two components at constant volume, ϕ_1 and ϕ_2 are the volume fractions of the components, and V_m is the average molar volume based on the molar fraction.

As the volume change of mixing is assumed to be zero, we obtain

$$\Delta H_1^\infty = V_1^\circ(\delta_1 - \delta_2)^2 \tag{25}$$

where ΔH_1^∞ is the partial molar heat of mixing.

If the pressure is constant, then

$$\Delta G_1^\infty = V_1^\circ(\delta_1 - \delta_2)^2 \tag{26}$$

Values of ΔG_1^∞ are easily obtained from Equation 8, and after rearrangement of Equation 26, $[\delta_1^2 - (\Delta G_1^\infty/V_1^\circ)]$ may be plotted vs. δ_1 and a linear relationship is obtained. The estimation of the slope enables calculation of the δ_2 value.

DiPaola-Baranyi and Guillet[3] reported that better results were obtained from a procedure based on the use of the interaction parameter. Fernandez-Sanchez et al.[52] found both sets of δ_2 values to be very close to each other.

D. Acceptor-Donor Interactions at the Interface

Fowkes[58] has proposed acid-base interaction heat (ΔH^{ab}) as a quantitative parameter of these interactions at the polymer interface. Chen[16] has suggested that ΔH^{ab} can be calculated from the heat of adsorption at the infinite dilution region. To eliminate the contribution of the solution process in bulk polymer, he used data below the glass transition temperature, T_g. Following Fowkes' theory, Chen assumed that polymer interfacial interactions could be divided into only two terms: dispersion and acid-base. Hydrogen bonding interactions were included in the acid-base term, and dipole-dipole interactions often seemed to be negligible. The acid-base interaction heat can be described by Drago's four-parameter empirical equation:

$$-\Delta H^{ab} = C_aC_b + E_aE_b \qquad (27)$$

where C_a and E_a correspond to each acid (polymer or probe, respectively), while C_b and E_b correspond to the respective bases. In general, C denotes the polymer, blend, or surface to be characterized, and E denotes the testing solute probe.

ΔH^{ab} was calculated from the relationship

$$-\Delta H^{ab} = -\Delta H - \Delta H_1 - \Delta H_2 + \Delta H^d \qquad (28)$$

where ΔH is the adsorption heat, ΔH_1 is the latent heat of vaporization, ΔH_2 is the heat expanded on the formation of a vacancy in the stationary phase for a solute probe molecule, and ΔH^d is the dispersion component of the probe-phase interaction heat.

Chen confirmed the validity of Fowkes' theory and the applicability of Equation 27. He also proposed a procedure for calculating Drago's parameter for any polymer or solute probe.

E. Characterization of Fibers

Grenier-Loustalot et al.[29] used the IGC technique to determine the surface properties of oxidized and sized carbon fibers. They overcame several technical difficulties, particularly in the construction of an appropriate chromatographic column. However, they used a terminology that could be misleading. For example, the term *solubilization chromatography* was used as synonymous with gas-liquid chromatography. The term *solubilization* is connected with the properties of micellar systems and describes the phenomenon of apparent solution of small amounts of the hydrophobic compound. The probe (solute) in gas-liquid chromatography is retained by its interactions with the bulk (or thin-film) stationary (liquid) phase. No solubilization process occurs, per se, and the terms *solution* or *sorption* are commonly used.[62,87-90] Investigators should consider at least three types of interactions that are important in the systems examined: (1) sorption in the sized areas, (2) adsorption at epoxy (epoxy-polyester)/gas interfaces and (3) adsorption on uncoated fibers. The last type of interaction seems to be particularly important, as the amount of surface modifiers (liquid-coated areas) was low (1%). The use of the expression *retention volume of a solution* was also unfortunate, as the authors[29] expressed it by the equation

$$V_R' = K_AA + K_LV_L \qquad (29)$$

where K_A and K_L are partition coefficients. A is the surface area of the free fiber, and V_L is the volume of the material. However, Equation 29 usually refers to V_N, the net retention volume:[62,87-95]

$$V_N = K_LV_L + K_IA_I + K_SA_S \qquad (30)$$

The authors considered the adsorption on uncoated fiber but appeared to overlook the interactions at the gas-liquid interface. In this particular case, it is possible that the solvent cannot be treated as a bulk liquid. It seems that the depth of the liquid phase is much lower than the "surface layer" — the distance from the surface to the point at which the influence of the support surface extends.[62,88,92] There are no data on the distribution of the modifier on the fiber surface,[29] but a simple calculation gives an indication that probably an average layer thickness exists that ranges from a monolayer to relatively thick droplets or layers. This means that a true bulk solvent may not exist at low loadings. The chemical component used as a testing probe is usually termed a *solute* or and *analyte*. The term *solvent* refers to the liquid stationary phase.

Grenier-Loustalot et al.[29] transposed the Langmuir equation to the conditions of chromatography as

$$C_L = \frac{K^\circ C_g}{1 + \beta C_g} \qquad (31)$$

This expression permits calculation of K° and β. If $\beta > 0$ and C_g is very large, the following relationship is approximated:

$$C_L^\infty = \frac{K^\circ}{\beta} \qquad (32)$$

where C_L^∞ is the maximum concentration that the carbon fiber can adsorb (i.e., the constitution of a monomolecular layer[29]) and K° is the partition coefficient for a null injected quantity of the solute. The BET equation was used in the case of S-shape isotherms in the form

$$C_L = V_m \frac{C*C_g}{(C_g^\circ - C_g)[1 + (C-1)C_g/C_g^\circ]} \qquad (33)$$

where V_m is the volume adsorbed if the entire surface of the solid is covered with a monolayer, C is the BET constant, and C_g° is the maximum concentration corresponding to the saturation vapor pressure of the solution.

The authors[29] characterized the examined fibers by K° values and the β term of the Langmuir equation. Grenier-Loustalot et al.[97] also used IGC to examine the kinetics of isothermal cross-linking in the polycondensation of epoxy-polymers with aromatic amines. Gas chromatographic results provide a gel point and a gelling range for the systems investigated.

Short glass fibers were examined by Saint Flour and Papirer.[133] They characterized the fibers' properties by parameters that will be described in Section G, which deals with modified silicas.

F. Polarity Parameters

There are a number of papers that report on the properties of surfactants and extractants examined by the inverse gas chromatographic method.[42-51,98-103] The properties of surface-active agents, as well as the efficiency of extractants, depend on their activity at oil/water interfaces.[104-107] Inverse gas chromatography was chosen as a method that provides a simple procedure and accurate and reliable quantitative parameters of the polarity of surfactants. He divided them into two groups: (1) empirical polarity parameters (e.g., polarity index) and (2) parameters having a physical meaning (thermodynamic functions of solution, partial molar excess Gibbs properties of solution, criterion A). The advantages and restrictions in using these parameters were discussed.[51] Generally, measurements of surfactants' polarities by means of gas chromatography express their hydrophile-lipophile balance. A number of empirical relationships were evaluated between the surfactants' properties and their polarity parameters. These relations were used to predict the properties of the examined compounds. The polarity parameters were also estimated with reasonable accuracy from values of structural increments for characteristic fragments of the molecules. The polarity parameters were used[104-107] to discuss the behavior of extractants and surfactants at liquid/liquid interfaces.

G. Modified Silicas

Papirer et al.[31-35] characterized the surface properties of different types of silicas modified by esterification of their surface silanol groups with alcohols, diols, poly(ethylene glycols), and their oligomers. They used inverse gas chromatography at zero surface coverage and at finite concentrations.

1. Adsorption at Infinite Dilution

The standard free energy of transferring a mole of vapor from the gas phase to a standard state on the surface is given by

$$\Delta G^\circ = -RT \ln \frac{B*V_N}{S*g} \qquad (34)$$

where $B = 2.99 * 10^2$ (according to the deBoers definition of the surface pressure in the adsorbed state), S is the specific surface area of adsorbent [m^2/g], g is the mass of the adsorbent in the column [g], and V_N is the net retention volume [m^3].

The authors identified ΔH as the differential heat of adsorption of the solute and estimated it from

$$\Delta H = R \frac{d(\ln V_N)}{d(1/T)} \qquad (35)$$

Hence,

$$\Delta S = \frac{\Delta H - \Delta G^{\circ}}{RT} \qquad (36)$$

Adsorbate-adsorbent interactions can be either dispersive (non-specific) or polar (specific). A similar situation was reported for solute-polymer interactions.[16] Thus, the surface free energy of an adsorbent is

$$\gamma_s = \gamma_s^d + \gamma_s^{spe} \qquad (37)$$

where d is dispersive and spe is the specific interaction.

The free energy of adsorption of alkanes varies linearly with the number of carbon atoms in their chemical structures, and the appropriate free energy of adsorption increment for a methylene group can be estimated from

$$\Delta G_{CH_2} = -RT \ln \frac{V_{N_n}}{V_{N_{n+1}}} \qquad (38)$$

Dorris and Gray[108] proved the validity of the following relationship:

$$\Delta G_{CH_2} = 6.023*10^{23}*a_{CH_2}*2[\gamma_s^d \gamma_{CH_2}]^{1/2} \qquad (39)$$

where a_{CH_2} is the surface area of a methylene group (0.06 nm^2), and γ_{CH_2} is the increment of surface tension for a methylene group [35.6 mJ/m^2]. The utilization of Equations 38 and 39 allows one to calculate the dispersive component of the surface free energy of silica (modified silica).

For polar probes,

$$\Delta G^{\circ} = \Delta G^d + \Delta G^{spe} \qquad (40)$$

and the adsorption of a polar molecule will be associated with a free-energy increment ΔG^{spe} (equal to $\Delta G^{\circ} - \Delta G^d$). Vidal et al.[31] pointed out that ΔG^{spe} would not provide an absolute measure of a specific adsorbate-adsorbent interaction but should be understood as an estimate of the magnitude of specific interactions between the surface and polar probes. Free-energy increments can be related to electron-donor (DN_B) and electron-acceptor (AN_E) numbers of a given solute as

$$\Delta G^{spe} = C_S^* \, DN_B + C_S'^* \, AN_E \qquad (41)$$

Two independent terms are necessary to describe specific interactions, as most solid surfaces exhibit an amphoteric behavior. C_s and C_s' represent the ability of the solid surface to undergo specific interactions — electron acceptance or donation, respectively. A set of experiments for a series of solute test probes whose electron-donor and electron-acceptor numbers are known allows for an estimation of both parameters for a given surface.

Inverse gas chromatography was used by Chapel and Williams[109] to measure the poly(phenylene terephthalamide) (PPTA) fiber surface cleanliness. The authors measured the surface adsorption of *n*-alkane vapors at infinite dilution over a range of temperatures. They calculated the differential heat of adsorption from

$$-\Delta H_A^{\circ} = R \frac{d(\ln K_S)}{d(1/T)} \qquad (42)$$

and the standard molar free energy of adsorption ΔG_A° from

$$\Delta G_A^{\circ} = -RT \ln \frac{K_S p_{s,g}}{\pi_s} \qquad (43)$$

where K_s is the adsorption partition coefficient, A is the surface area [m^2], $p_{s,g}$ is the reference pressure (101.3 kN/m^2), and π_s is the two-dimensional surface pressure (0.338 mJ/m^2). The standard entropy of adsorption ΔS_A° was established from the Gibbs relationship. The London (dispersive) component of the surface free energy of interaction (γ_s^d) was calculated from Equation 39 using γ_{CH_2} = 37.5 mJ/m^2.

2. Adsorption at Finite Concentration of Solute

Papirer et al.[32] reported the characterization of some initial and modified (grafted) silicas at finite solute concentrations. The appropriate adsorption isotherms, a = f(P), were calculated from chromatographic data using

$$a = \frac{1}{mRT} \int_o^P \frac{V_N}{1 - B} dP \qquad (44)$$

and

$$P = \frac{VURTh}{\overline{V} D_S S_P} \qquad (45)$$

where m is the mass of adsorbent in the column, V_N is the retention volume of the solute probe, B is the correction factor for the sorption effect, R is the gas constant, T is the column temperature, V is the volume of solute injected, $\overline{V}$ is the solute molar volume, U is the speed of the recorder chart, D_s is the average gas flow at column temperature T, S_P is the area of the peak for the injected volume of solute, and h is the height of the chromatographic peak. The monolayer coverage and C values were calculated from the well-known BET equation

$$\frac{P}{a(P_o - P)} = \frac{1}{a_o C} + \frac{C - 1}{a_o C} \frac{P}{P_o} \qquad (46)$$

where a is the concentration of adsorbed solute at relative pressure P/P; a_o is the monolayer coverage, and C is the BET constant.

The differential (isosteric) heat of adsorption was calculated from the following relationship:

$$\Delta H_a = R \left[\frac{\delta \ln P}{\delta(1/T)} \right]_\theta \qquad (47)$$

under the assumption that the isotherms were obtained at small temperature intervals. The evaluation of ΔH_a as a function of changes in the surface covering ratio could provide information about the solid surface under study.

Vidal et al.[32] used the spreading pressure π_e

$$\pi_e = \int_o^{P=1} \frac{a}{A} \frac{dP}{P} \qquad (48)$$

where A is the surface area of adsorbent, as a parameter that can describe the effect of the grafted alkyl chains on adsorbate-asorbent interactions.

The difference between the chemical potentials of a polar (benzene, B) and a nonpolar (*n*-hexane, H) solute adsorbed under identical conditions is related to the surface polarity of the solid.[32] Such a parameter was used to evaluate the surface polarity after treatment of the surface of the sample, as

$$\begin{aligned} \Delta(\Delta\mu^{ads}) &= \Delta\mu^{ads}_{(B/H,s,a)} - \Delta\mu_{(B/H)} \\ &= RT \ln\left[P_{(B,s,a)}/P_{(H,s,a)} \right] \end{aligned} \qquad (49)$$

III. EXPERIMENTAL

A. Equipment

Commercial gas chromatographs equipped with FID[3,8,10,15,17,29,31] and/or TCD[15,17,29] were used in the IGC experiments. Packed stainless steel or copper columns, 30 to 160 cm long by 0.2 to 6 mm I.D., were filled with (1) commercial supports coated with polymers, their blends, or surfactants; (2) initial or modified silicas; or (3) short glass fibers. A special column was developed for the study of the surface properties of carbon fibers.[29] The column was composed of three "cell" sections. each section contained (1) a tube 15-cm long by 0.7-cm wide and a 1-cm deep cavity; (2) a Teflon gasket; and (3) a cover. Each cell was filled with pieces of fiber that were cut to the length of the cavity. The carrier gas line was fitted with a sintered glass disk placed into the inlet and outlet of each cell. Proper filling of the column was verified by dead volume measurements.

Anthony and Holland[110] modified a dual-oven gas chromatograph for surface characterization purposes. They connected two columns placed in two separated chambers of the oven by a pneumatic valve. They also equipped the chromatograph with an additional detector after the first column. The first-reference column separated the components of the test mixture into a series of single symmetrical peaks. If the second column (the tested column) is inert, the components of the test mixture would elute in the same order without changes in their relative retention times. The chromatographic activity of a noninert tested column would produce changes in the peak profiles, their areas, and their relative retention times.

Such changes provide information on the nature and power of the interactions of the test solutes with the examined material. The authors[110] summarized the advantages of their studies as follows: (1) test and reference chromatograms are obtained in parallel, permitting an "on-line" monitoring of the tested column and determination of the adsorption effects that could be immediately separated from disturbances caused by an improper injection of solutes, solute probe decomposition, etc.; (2) changing the solute probe composition or the chromatographic conditions does not require removing both columns and installing a single reference column (as in the traditional method); and (3) isothermal or programmed temperature procedures could be established independently for both columns to reach optimum conditions. Anthony and Holland utilized this system for the characterization of gas-solid interfaces. However, it seems that such a system would be quite useful in all IGC experiments.

B. Column Preparation

The column packing was prepared in the traditional way, i.e., the stationary phase was dissolved in a suitable solvent and deposited onto an inert support by slow evaporation of the solvent with gentle stirring and heating.[3,10-13,15,18,22,28,42-50,52,62,66-73,76,96,111,112] However, in the case of polymers and their blends, part of the material is deposited on the glassware. The actual amount of coated polymer was established by calcination[113] or Soxhlet extraction.[15] Fried and Su[27] observed that methyl-group-substituted aromatic polymers [e.g., poly(2,6-dimethyl-1,4-phenylene oxide)], can be removed only partially (<47%) by Soxhlet extraction of IGC column packings after high-temperature runs. Column loadings determined in this way could be significantly lower than their actual value. Edelman et al.[13,14] estimated the exact column loading by thermogravimetry using the required blank correction. Al-Saigh and Munk[5] proposed another method involving the addition of part of the polymer solution to the support, followed by drying and mixing the powder. The procedure was repeated until all the solution, including rinsing of the solution flask, was added. These authors[5] found that their soaking method provided an excellent accuracy for the determination of the mass of the polymer coating. They used this procedure in most of their work.[5,6,8,17,18] In the case of polymer blends used as stationary phases, special care should be taken to avoid the demixing of polymers during the evaporation of the solvent. Wang and Charlet[15] indicated that the soaking procedure generates a distribution of thickness of polymer film that is likely to be nonuniform. However, the authors did not estimate the magnitude of this effect and its influence on retention data. They suggested a procedure that combines the two methods mentioned above. In any case, the solvent residue was removed from the polymer-coated support by drying in a vacuum oven at 100°C for 12 h to 3 d.

The carbon fibers, after modification of their surfaces,[29] were cut to the length of the cavity of the special column. Each cell was completely filled with pieces of fibers to decrease the dead volume of the column. Saint Flour et al.[136] placed short glass fibers having a mean diameter 0.5 to 1.0 mm into a 1-m long by 6.35 mm O.D. steel column.

The procedure used by Vidal et al.[31] is a good example of preparing a column filling for inverse gas-solid chromatography. The first step was the modification of the silica surface by esterification with an appropriate reagent. Agglomeration carried out under pressure (10^9 Pa) was followed by sieving to recover particles of 0.2 to 0.5 mm. Such particles were used to fill the chromatographic column. In the determination of the properties of heavy residues of oil distillation, the deactivated silica support was impregnated with the testing material.[55] The dried silica was placed into a typical chromatographic column.

C. Test Solutes

A wide range of chemical compounds have been used as test solutes in IGC experiments. They were either injected individually or as test mixtures. Table 1 shows exemplary test solutes. The selection of test solutes should be carried out

TABLE 1
Test Solutes Used in IGC Experiments

Solute	Ref.
n-Alkanes	3, 8, 10, 17, 24, 26, 29, 31–33, 35, 42–50, 98–103
Cycloalkanes	55
Alkenes	8
Chloroalkenes	8, 10, 18, 26, 31, 32, 35, 55
n-Alcohols	18, 28, 29, 35, 42–50, 52, 98 103
Ketones	8, 17, 18, 26, 28, 31, 44–50, 52
Alkyl esters	8, 17, 18, 26, 28, 31, 55
Tetrahydrofurane	8, 17, 31, 32, 35
Dimethylformamide	10
Ethers	10, 28, 31, 32, 35, 55
1,4-Dioxane	10, 17, 26
Nitriles	31, 55
Dimethylsulfoxide	28
Benzene	3, 17, 18, 26, 27, 31, 32, 35, 44–50, 52, 55
Toluene	3, 17, 18, 26, 27, 35, 55
Other alkylbenzenes	3, 27, 29, 31, 55
Chlorobenzene	10, 18, 27
Pyridine	44–50, 52

so as to obtain a group of analytes that could be used to evaluate all important properties of the examined material. This means that the test solutes selected should provide all possible types of interactions with the column filling. However, the selection of solutes in each particular case depends on the knowledge and interest of the chromatographer.

D. Data Reduction

The first problem to be considered in this section is the specific retention volume. This retention parameter is used in the basic Equations 2 and 8 when polymers or their blends are examined. The symbol V_g° in these relations represents the net retention volume of a solute at column temperature T_c per gram of liquid phase, adjusted to a standard state of 0°C (273.13 K).[1] Paterson et al.[1] derived Equation 8 using this definition of the specific retention volume. This was also used by Conder and Young.[114] However, several authors calculated the specific retention volume as the ratio of the net retention volume and the mass of the stationary phase:

$$V_g = \frac{V_N}{w} \qquad (50)$$

without an adjustment to 273.15 K.[8,18,22,111] Others converted the ratio V_N/w to room temperature.[5-7,17,27]

The column dead time was measured as the air peak retention time[17] or was calculated from retention times of *n*-alkanes[8] (e.g., by the use of the Grobler-Balizs procedure[44-50]).

At least two effects can influence retention data in IGC experiments: adsorption at the gas-liquid interface and adsorption on the solid support. V_N often depends also on the flow rate of the carrier gas. To compensate for slow establishment of phase equilibrium retention values, data were extrapolated to the zero flow rate of the carrier gas.[7,8,15,17,105,115] Cheng and Al-Saigh[17] found that this procedure could contribute to a large error if the carrier gas was helium. However, Wang and Charlet[15] pointed out that (1) the flow rate dependence is not necessarily linear and (2) there is no theoretical basis for an extrapolation to a zero flow rate. As a consequence, it is not obvious whether thermodynamic parameters that are actually free from all kinetic factors can be obtained by this procedure. Bhattacharya et al.[18] found only a small, random variation of V_g° with changes in the carrier gas flow rate. They concluded that the observed effect is attributable to experimental error and that V_g° is independent of the flow rate. They used averaged V_g° values, which were not extrapolated to a zero flow rate.

To adjust for any contribution of solute-solid support interactions to V_g° values, the specific retention volumes of the probes were often corrected by subtracting the retention of the given probe on the uncoated support from the crude (apparent) specific retention volume.[6,17,78] However, retention data observed on uncoated supports are the result of the solute's interactions with all free, accessible sites on the support surface. In coating the support with the liquid phase, this free support area rapidly decreases and so does the contribution of solute-support interactions to V_g° values. The support contribution was reported to be as high as 5 to 30% of the V_g° value.[6,8,17] However, it seems that this effect is relatively lower, depending on the degree of surface coverage in the liquid phase, and does not exceed several percent of V_g°. Careful support deactivation or the increase of liquid loading minimizes this undesirable effect, but the significance of adsorption at the support interface cannot be ignored.[62,76] Chapel and Williams[109] corrected specific retention volumes for the influence from solute interactions with the walls of a chromatographic column. They measured the net retention volumes of the test solutes on an empty column and subtracted these values from apparent specific retention volumes.

In IGC measurements, peak asymmetry has almost always been observed.[76,114,116,117] Computer simulation of IGC results by Munk et al.[25,118] predicted that a significant asymmetry is always to be expected, even when equilibrium is reached instantaneously. The fact that statistical moments of peaks are the only accurate measures of retention and peak broadening is still not sufficiently popular among researchers.[15,76,114,117-118] However, very often in the case of asymmetrical peaks, authors followed procedures suggested by Conder and Young.[114] Jönsson[74,75] studied the problem of correctly measuring retention times in linear, nonideal elution chromatography. He examined relationships between three different retention measures (the maximum of the peak, the median, and the center of gravity) and the skew and width of the observed elution peaks. For symmetrical peaks, these three measures of retention time are identical; but for nonsymmetrical peaks, the degree of skew usually depends on the nature of the peak broadening mechanism. Jönsson found the median as the correct measure of the retention time (volume). Voelkel[76] used these three measures of retention time to calculate three sets of polarity parameters. These were generally similar for alcohols (standard solutes), as the observed differences were random and statistically insignificant. However, differences in the retention time and retention index of pyridine were high, systematic, and significant on all examined stationary phases.

IV. REPORTED RESULTS

A. Polymers

1. Thermodynamic Parameters

DiPaola-Baranyi and Guillet[3] determined weight fraction activity coefficients, thermodynamic functions of mixing, and Flory-Huggins interaction parameters for a series of hydrocarbon solutes on poly(methyl acrylate). They found that the activity coefficients decreased with increasing temperature, which is related to the increasing solubility of the solutes in the polymer. The activity coefficients increased with an increase in the carbon number of the alkanes.[3,52] The composition of the stationary phase (polymer blend) significantly influenced the value of this parameter. The activity coefficients for nonpolar probes (*n*-alkanes) increased with an increase in the content of the more polar component in the mixture, indicating that their solubility in the blend examined decreased.[52] For polar solute probes, one can observe the opposite relationship.[52]

The values of ΔH_1^∞ calculated from Equation 10 varied for aromatic solutes from 0.3 to 1.1 kcal/mol in poly(methyl acrylate), and from −0.01 to 0.3 in polystyrene.[3] The corresponding values for saturated hydrocarbons were 2.5 to 4.1 and 0.5 to 2.5 kcal/mol for the two polymers, respectively. The authors[3] indicated that these trends were expected for solvent-polymer and nonsolvent-polymer systems. A general increase in ΔH_1^∞ values was observed with an increase in the hydrocarbon chain length for *n*-alkanes and *n*-alkyl substituted derivatives of cyclohexane and benzene.

Irribarren et al.[10] correlated experimental values of ΔH_1^∞ with solute probe polarizabilities, P: dipole moment, μ; and Taft's empirical parameters, β, for probe hydrogen-bond accepting power, according to the equation

$$\Delta H_1^\infty = aP + b\mu + d\beta \qquad (51)$$

These authors reported good agreement in ΔH_1^∞ values calculated from Equation 9 with those obtained experimentally for poly (*N*-vinyl pyrrolidone)/phenoxy resin and tetramethylene sulfone/phenoxy resin systems.

The partial molar free energies of mixing ΔG_1^∞ (calculated from Equation 9) increased with an increase in the hydrocarbon chain of *n*-alkanes. The polar solutes were generally characterized by decreasing values of ΔG_1^∞ when the content of the more polar component of the examined blend increased. In such a case the respective values for *n*-alkanes significantly increased. However, the range and direction of change of ΔG_1^∞ also depends on individual properties of the polar component of the polymer blend. ΔG_1^∞ for 1-butanol decreased from 2096 cal/mol on OV-101 to 1467 cal/mol on Carbowax 20M. However, when a mixture of OV-101/OV-25 was examined, the values of ΔG_1^∞ changed from 2096 cal/mol for pure OV-101 to 2200 cal/mol for pure OV-25. The corresponding values for pyridine were 1504 and 1294 cal/mol, respectively.

The thermodynamic sorption parameters ΔG_1^s, ΔH_1^s, and $T\Delta S_1^s$ were determined for the process involving the transfer of solute molecules from the vapor phase into the amorphous portion of PVF2 [poly(vinylidene fluoride)].[17] Linear relationships were obtained between these parameters and the number of carbon atoms in homologous alkane and acetate series used as solute probes. The contributions of the methylene group in both probe series to ΔG_1^s, ΔH_1^s, and $T\Delta S_1^s$ values were attributed to van der Waals dispersive forces. The contribution of the CH_2 group to the partial molar heat of sorption was found to be -0.44 and -0.73 kcal/mol for the alkane and acetate series, respectively.[17] Chen and Al-Saigh attributed the difference in the contribution to interactions between the solvent and the methylene group for the two series of solute probes to the influence of the carbonyl group in the acetates. Hence, the difference in the $\Delta H_1^s(CH_2)$ values is associated with the difference in the structures of the interacting solute probes between the two series. However, the molecules of both series differ not by $C=O$, but by a $-COO-$ (carboxyl) group. It has been shown that the effect on the increments of the sorption parameters by carbonyl and carboxyl groups are significantly different.[119-121]

Chen et al.[17] assumed that ΔH_1^s (and other sorption parameters) are additive. Consequently, we have

$$\Delta H_1^s \text{ (alkanes)} = n\delta(\Delta H_1^s)_{CH_2 alk} \qquad (52)$$

and

$$\Delta H_1^s \text{(acetates)} = m\delta(\Delta H_1^s)_{CH_2 acet} + \delta(\Delta H_1^s)_{coo} \quad (53)$$

where $\delta(\Delta H_1^s)_{CH_2 alk}$ and $\delta(\Delta H_1^s)_{CH_2 acet}$ are the increments for the methylene group in the alkane and acetate probe series, respectively; $\delta(\Delta H_1^s)_{CH_2} = \delta(\Delta H_1^s)_{CH_3}$; and n and m are numbers of methylene and methyl groups in both probe series, respectively. Equations 50 and 51 show that the difference $[\delta(\Delta H_1^s)_{CH_2 alk} - \delta(\Delta H_1^s)_{CH_2 acet}]$ is not the measure of $-COO-$ (and, all the more, not of $C=0$) group contribution to the δH_1^s value. However, we can discuss it as a measure of the influence of the carboxyl group on the increment of the methylene group in the acetate series. This is additional evidence that all components of the solute molecule influence each other, their increment contribution to thermodynamic parameters depend on the position in the molecule, and that the additive rule should be used very judiciously.[62,122-124]

2. Flory-Huggins Interaction Parameter

The Flory-Huggins interaction parameter χ_{12}^∞ exhibits high values for a poor solvent used as an examined polymer or polymer blend,[10,11,13-14,52] while low values reflect good solubility capacities. For example, high values of χ_{12}^∞ for *n*-decane or tetradecane ($2.0 < \chi_{12}^\infty < 3.4$ at 80 to 160°C) indicate that these alkanes are very poor solvents for phenoxy resin.[10] Negative χ_{12}^∞ values found for the 1,2,3-propanetryil trinitrate (NGL)/α,ω-dihydroxy poly(tetramethylene carbonate) and the NGL/α,ω-dihydroxy poly(oxyethylene) systems (Table 2) indicate good solubility of NGL in both polymers.[14] These values were significantly lower than those obtained for 1,2,3-propanetryil triacetate (TA),[14] indicating that NGL is a better solvent than TA for the examined polymers. For semicrystalline poly(vinylidene fluoride) alkyl, acetates are much better solvents ($\chi_{12}^\infty \cong 0$) than *n*-alkanes, which

TABLE 2
Flory-Huggins Interaction Parameter Values for Triacetin (TA) and 1,2,3-Propanetryil Trinitrate (NGL) at Infinite Dilution in Polyoxyethylene (9) and in Poly(Tetramethyl Carbonate) (7) at 431.1 K and Extrapolated to 298.1 K[14]

	χ_{12}^{∞}	
Solute/Polymer	298.1 K	431.1 K
TA/7	1.37	0.23
NGL/7	1.71	−0.50
TA/9	0.70	0.07
NGL/9	0.69	−0.72

exhibit much higher interaction coefficients.[17] In a series of *n*-alkanes, χ_{12}^{∞} increased with an increase in the number of carbon atoms in the alkane molecule.

The solute/polymer interactions parameter χ_{12}^{∞} decreases with temperature for those systems that exhibit an upper critical solution temperature (UCST)[10,11,13,17] (e.g., 1,2-dichloroethane/phenoxyresin,[10] triacetin (TA)/α,ω-dihydroxy poly(oxyethylene),[13] or chloroform/atactic polystyrene[11] systems). All such relations are parabolic,[10,11,13,14,17] and in most cases a minimum is observed, which indicates the temperature of the highest mutual miscibility of the solute and polymer.[10,13] The observed parabolic relationship was explained on the basis of a lattice model.[11] Lattice-fluid theory[82-84] relates such behavior to a simultaneous decrease of the enthalpic contribution.

$$\chi_H = -T\frac{\delta\chi}{\delta T} \tag{54}$$

and an increase in the entropic contribution;

$$\chi_s = \frac{\delta(T\chi)}{\delta T} \tag{55}$$

with increasing temperature.

The parabolic temperature dependence of χ_{12}^{∞} has been shown experimentally for several systems.[10,11,19-14,17,125-126] Uriarte et al.[11] described the χ_{12}^{∞} vs. temperature relationship according to the equation:

$$\chi_{12}^{\infty} \equiv g^{\infty} = \frac{B_o + B_1T}{(1-\gamma\phi_2)} + a_1 + a_2T \tag{56}$$

where g^{∞} is the interaction function in terms of the interchange energy; at infinite dilution $\chi_{12}^{\infty} \rightarrow g^{\infty}$; $\gamma = 1 - \alpha_2/\alpha_1$, and α_2/α_1 is the ratio of the surface areas of the polymer segments and the solvent molecules calculated from Bondi's radii; ϕ_2 is the volume fraction of the polymer; and B_0, B_1, a_1, and a_2 are constants.

Following Koningsveld,[127] Uriarte et al.[11] separated g^{∞} into two contributions: g_H^{∞} related to an enthalpic term and to an entropic contribution

$$g^{\infty} = g_H^{\infty} + g_S^{\infty} \tag{57}$$

Values for g_H^{∞} and g_s^{∞} are available from IGC measurements.

Fernandez-Sanchez et al.[52] calculated the enthalpic and entropic contributions to the solute-polymer interaction parameter from Equations 22 and 23. Such data for mixtures of OV-101/Carbowax 20M are presented in Table 3. In all examined systems of mixed stationary phases, significant differences were found between the χ_s^{∞} values calculated from both equations. It was indicated that χ_s^{∞} from Equation 23 is more reliable.[52] For solutes and polymers of similar chemical structure, χ_H^{∞} is small, and $\chi_H^{\infty} < \chi_s^{\infty}$. Values of χ_H^{∞} for *n*-alkanes on OV-101 are small and increase with an increase in the polarity of the mixed stationary phase. For polar polymers, polar solutes exhibit a small enthalpic contribution to the interaction parameter. If the polarities of the solute and stationary phase are different, the enthalpic contribution becomes more important. The authors[52] indicated that the values of δ_1 and δ_2 may qualitatively describe the relative values of χ_H^{∞} and χ_s^{∞}, although the prediction of χ^{∞} seemed to be impossible. They followed Price et al.[72] and proposed a correction to the solute-polymer interaction parameter due to pressure-volume effects, as

$$\chi^{\infty} = \chi_H^{\infty} + \chi_S^{\infty} + \chi_{pv}^{\infty} \tag{58}$$

TABLE 3

Enthalpic (χ_H^∞) and Entropic (χ_S^∞) Contributions to the Solute-Polymer Interaction Parameter at 393 K[52]

		$\phi_{OV\text{-}101}$				
Contribution	**Compound**	**1**	**0.757**	**0.509**	**0.257**	**0**
χ_H^∞	*n*-Hexane	0.063	0.165	0.456	0.880	1.605
	n-Heptane	0.007	0.060	0.275	0.633	1.290
	n-Octane	0.000	0.026	0.205	0.543	1.194
	n-Nonane	0.010	0.006	0.145	0.458	1.098
	n-Decane	0.034	0.000	0.099	0.388	1.017
	n-Undecane	0.065	0.004	0.069	0.339	0.966
	n-Dodecane	0.078	0.007	0.066	0.346	1.007
	Benzene	0.261	0.150	0.029	0.002	0.092
	1-Butanol	1.424	1.145	0.731	0.416	0.146
	2-Pentanone	0.211	0.104	0.007	0.021	0.189
χ_S^∞	*n*-Hexane	0.264	0.502	0.634	0.684	0.609
	n-Heptane	0.283	0.538	0.678	0.732	0.652
	n-Octane	0.309	0.588	0.742	0.801	0.713
	n-Nonane	0.336	0.640	0.807	0.872	0.776
	n-Decane	0.364	0.692	0.873	0.942	0.839
	n-Undecane	0.392	0.746	0.941	1.016	0.904
	n-Dodecane	0.421	0.801	1.010	1.091	0.971
	Benzene	0.170	0.323	0.408	0.440	0.392
	1-Butanol	0.168	0.320	0.404	0.436	0.388
	2-Pentanone	0.204	0.389	0.490	0.529	0.471

3. Solubility Parameters

DiPaola-Baranyi and Guillet[3] measured solubility parameters for polystyrene and poly(methyl acrylate) using Equations 23, 25, and 26. Solubility parameters for polystyrene and poly(methyl acrylate) estimated by IGC were 7.6 ± 0.2 and 8.7 ± 0.3 at 193°C and 100°C, respectively. They indicated that free-energy relationships give better correlations (Equations 23 and 26) with solubility parameters than enthalpies alone. The interaction parameter χ^∞ is a Helmholtz free energy — the work function relating the free energy required to remove a solute molecule from a polymer matrix at infinite dilution to that required to remove the same molecule from the pure solute at the same temperature.[3] This is a parameter of fundamental significance. DiPaola-Baranyi and Guillet showed that the infinite dilution polymer solubility parameters measured by inverse gas chromatography are useful in deriving fundamental information about polymer solubility. Ren et al.[28] found that values of the solubility parameter δ_2 for polyether gel obtained from IGC experiments agreed well with those measured with a Calvet microcalorimeter. They used δ_2 for judging the solubility between polyether gel and explosive solvents and for the selection of suitable energetic solvents.

Fernandez-Sanchez et al.[52] showed the variation of the solubility parameters with the composition of the mixed stationary phase (Figure 1). They found that only in some cases can the solubility parameters for mixtures of polymers be deduced as a linear combination of those for pure components.

Becerra et al.[128] reported solubility parameters for two silicone gas chromatography stationary phases OV-101 and OV-105 as 6.49 and 6.83 (cal cm^{-3}), respectively. The increase in δ_2 is connected with the presence of 5% of cyanopropyl groups in the dimethyl silicone. They found no temperature dependence of δ_2 for both examined polymers.

Fernandez-Sanchez et al.[129] examined three capillary columns of Superox 20M, two of which were immobilized in different ways. These workers were interested in the effect of immobilization on (1) the phase-transition temperature, (2) changes in the solubility parameter of the poly-

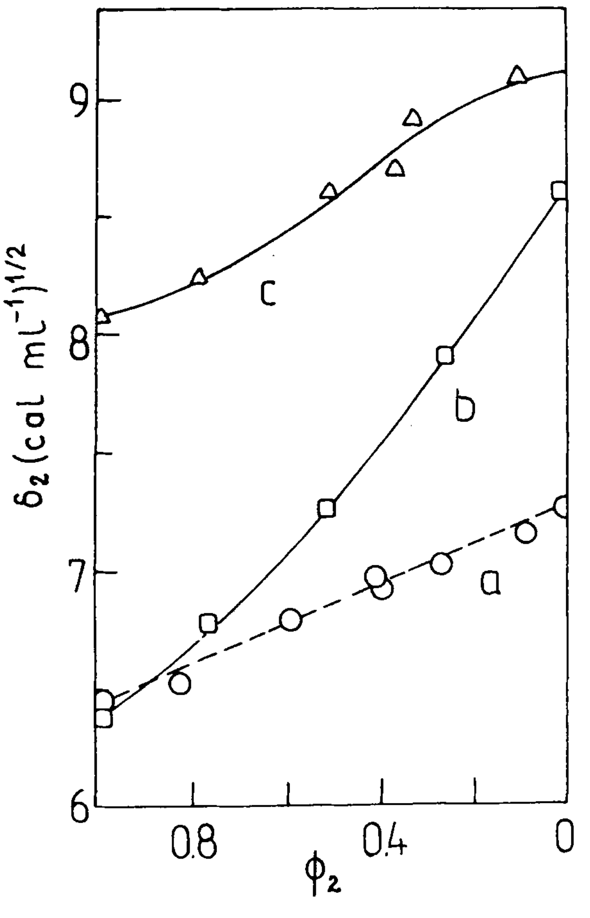

FIGURE 1. Variation of solubility parameter δ_2 of the stationary phase with mixture composition;[52] (a) OV-101/OV-25; (b) OV-101/Carbowax 20M; (c) OV-225/SP-2340. ϕ_2 represents the volume fraction of the first polymer in each instance. (From Fernandez-Sanchez, E., Fernandez-Torrez, A., Garcia-Dominquez, J. A., and Santiuste, J. M., *J. Chromatogr.*, 457, 55, 1988. With permission. © Elsevier Science Publishers, Physical Sciences & Engineering Division.)

mer, and (3) changes in the interaction parameters. They found that the nonimmobilized polymer has a higher solubility parameter than immobilized polymers. The small differences noted were caused by removing hydrogen bonding groups during the immobilization process. Solubility parameters of the stationary phases measured on the three columns decreased linearly with temperature.

Price[130] determined solubility parameters for compounds of relatively small molecular size. It was of interest to assess whether the assumptions made in the evaluation of δ_2 would be applicable to systems involving small molecules (e.g., polymer additives). He examined two nonpolar alkanes (*n*-hexadecane and squalane), two compounds having polar groups (*N*-methyl pyrrolidone and dibutyl-2-ethyl hexamide), and two alkyl phthalates (dinonyl phthalate and di-*n*-octyl phthalate). Plots using Equation 23 that give excellent linear correlations for polymers are not obeyed with these compounds. The curvature in the alkane systems was downward (lower estimates of δ_2), while the curvature for the more polar compounds was upward (overestimates of δ_2).

Price[130] attempted to separate the various contributions to the solubility parameter. The slopes from Equation 23 were calculated separately using aromatic and aliphatic probes. The latter of these was assumed to account for δ_d, while the difference between them was ascribed to δ_p. The value of the total solubility parameter was calculated from the equation

$$\delta^2 = \delta_d^2 + \delta_p^2 \qquad (59)$$

where δ_d is attributed to dispersive forces and δ_p to polar forces.

The prediction of δ for polar compounds was considerably improved by the proposed procedure.

Price indicated some nonsolved problems as (1) the "negative δ_p" values for squalane and hexadecane; (2) δ_p values derived from IGC refer to concentrated solutions, while other methods are often applicable to dilute solutions (the relationship between these values is unclear); and (3) the interaction parameter χ for small molecule systems may include contributions that are much less significant in polymer systems.

4. Polymer-Polymer Interaction Parameter

The polymer-polymer interaction parameter was established to describe the mutual miscibility of polymers. In most cases, the dependence of the χ'_{23} value on the chemical nature of the solute was reported.[8,12,18,24,27,52,111] Such dependence was discussed as an inadequacy of the Flory-Huggins model for the polymer-polymer-probe ternary system. This phenomenon has been interpreted as a result of preferential interactions involving solubility with one of the components of the blend.[12,52,77,115,131] Solutes with different chemi-

TABLE 4
Influence of the Probe and Mixture Composition on the Polymer-Polymer Interaction Parameter χ'_{23}

	OV-101/Carbowax 20M[a,b]			PCl/PECH[b,c]		
		$\phi_{ov\text{-}101}$			ϕ_{Pcl}	
Solute	0.757	0.509	0.257	0.75	0.50	0.25
n-Pentane	—	—	—	0.0	0.08	0.10
n-Hexane	0.476	0.503	0.582	0.06	0.08	0.10
n-Heptane	0.603	0.667	0.859	0.05	0.05	0.11
n-Octane	0.600	0.751	0.969	0.06	0.05	0.12
n-Nonane	0.675	0.845	1.163	0.06	0.05	0.12
n-Decane	0.718	0.914	1.330	—	—	—
Benzene	−0.651	−0.409	0.636	−0.20	−0.22	−0.19
Butyl chloride	—	—	—	−0.13	−0.16	−0.13
Chloroform	—	—	—	−0.06	−0.12	−0.09
1-Butanol	−0.378	0.063	0.159	—	—	—
1,4-Dioxane	—	—	—	−0.27	−0.29	−0.25
2-Butanone	—	—	—	−0.24	−0.24	−0.20
2-Pentanone	−0.906	−0.555	−0.534	—	—	—

[a] Ref. 52.
[b] ϕ = volume fraction.
[c] PCl = polycaprolactone; PECH = polyepichlorohydrin; see Ref. 8 and 26.

cal structures should behave differently in a mixture of polymers of very different polarity. Consequently, one class of solutes may exhibit linear behavior with a polymer mixture composition, while another solute class may show a nonlinear dependence when the same mixture of polymers is considered[52] (Table 4, Figure 1).

Price[130] suggested that large, positive values (>0.5) of this parameter indicate a strong interaction between the polymers; a low value represents little or no interaction, while a highly negative value indicates the presence of strong specific interactions (e.g., hydrogen bonding).

El-Hibri et al. reported that polymer-polymer interaction parameters and χ'_{23} and B_{23} are insensitive to both temperature and mixture composition for the system poly(caprolactone)/poly(epichlorohydrin) examined in the temperature range between 80 and 120°C.[8,26] However, Fernandez-Sanchez et al.[52] found significant changes in χ'_{29} with the polymer blend composition (Figure 2). Their results are supported by Nandi et al.[111] and DiPaola-Baranyi et al.[61] Data for the blends of poly(methyl acrylate) and poly(vinyl acetate) show the sensitivity of χ'_{23} to the chemical nature of the solute probe, the mixture composition, and the temperature of the experiment. Fried and Su[27] reported χ'_{23} data for blends of poly (2,6-dimethyl-1,4-phenylene ox-

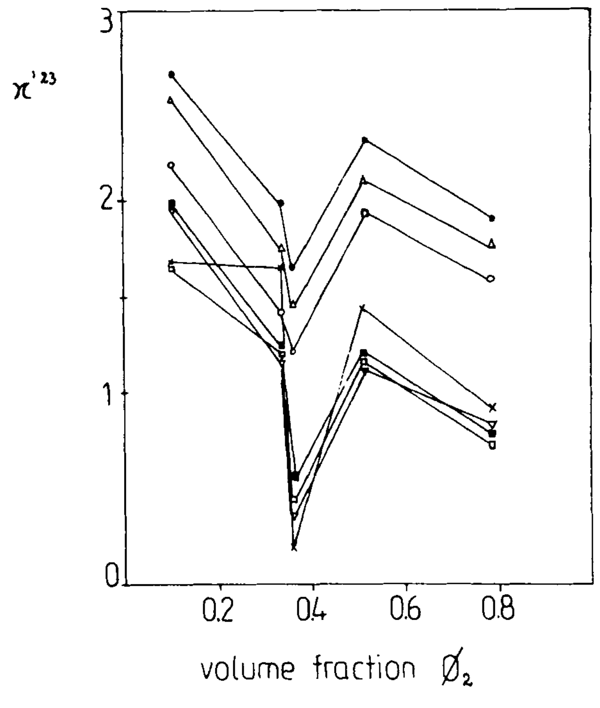

FIGURE 2. Dependence of polymer-polymer interaction parameter χ'_{23} on the test probe and mixture composition;[52] ○ = hexane; △ = octane; ● = decane; □ = benzene; ■ = 1-butanol; × = 2-pentanone; ▽ = pyridine. (From Fernandez-Sanchez, E., Fernandez-Torrez, A., Garcia-Dominquez, J. A., and Santiuste, J. M., *J. Chromatogr.*, 457, 55, 1988. With permission. © Elsevier Science Publishers, Physical Sciences & Engineering Division.)

ide) (PMMPO) with polystyrene (PS) and with poly(4-methylstyrene) (P4MS). They found that $\varkappa'_{23}$ is very stable for different solute probes (benzene, toluene, ethylbenzene, chlorobenzene, and bromobenzene) in the PMMPO/PS system. They calculated an average $\varkappa'_{23}$ value for all the probes as -0.45 ± 0.03 (at 260°C). However, for the PMMPO/P4MS system, $\varkappa'_{23}$ values vary significantly, and the average value is characterized by an extremely high standard deviation (i.e., -0.15 ± 0.11).

Elorza et al.[12] used the temperature dependence of $\varkappa'_{29}$ (Figure 3) to study the miscibility of the polystyrene/poly(methyl vinyl ether) system (PS/PMVE). They found the phase-separation temperature in two ways: (1) at the point of intersection of straight lines of ln V_g vs. 1/T obtained in the range of temperatures below and above the separation temperature; and (2) by the use of the $\varkappa'_{23}$ parameter. At the phase-separation temperature, $\varkappa'_{23}$ should be close to zero when the molecular weights of the polymeric components are sufficiently high. The results obtained by two methods agree well within the limits of experimental error.[12] According to these criteria, the phase-separation temperature of the PS/PMVE (50/50 wt/wt) system was reported to be within the range of 115 to 120°C.

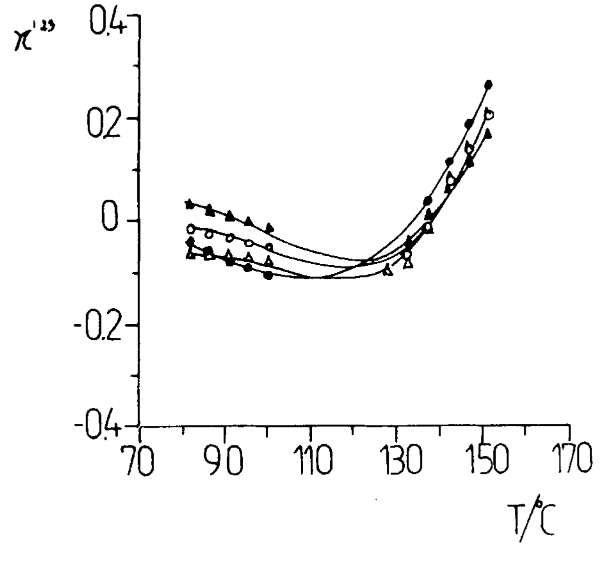

FIGURE 3. Temperature dependence of polymer-polymer interaction parameter $\varkappa'_{23}$;[12] ▲ = chlorobenzene; △ = benzene; ○ = toluene; –1-Propanol; 50:50 (wt) PS/PMVE system with a loading 7.5 wt%. (From Elorza, J. M., Fernandez-Berridi, M. J., Iruin, J. J., and Uriarte, C., *Makromol. Chem.*, 189, 1855, 1988. With permission © Hüthig & Wepf Verlag, Basel.)

5. Degree of Crystallinity of Polymers

Inverse gas chromatography was also used to determine the crystallinity of polymers.[17,24,61,133-135] The general assumption made for the determination of polymer crystallinity by IGC is that the solute probe molecules interact only with the amorphous polymer; the crystallinity regions are assumed to be impenetrable.[24] The retention volume (time) depends on the amount of the amorphous material present on the column:

$$V_g^o = (1 - C)V^o_{g\ \mathrm{amorph}} \qquad (60)$$

where c is the fraction of crystalline polymer and $V_{g\ \mathrm{amorph}}$ is the retention volume for a totally amorphous polymer.

By extrapolation of the linear portion of the retention diagram, ln V_g vs. 1/T (above T_m), to lower temperatures, one can calculate the retention volume V_g^{o*} that corresponds to a hypothetical, completely amorphous, polymer below T_m (at a given temperature). The ratio of the measured V_g^o to the extrapolated V_g^{o*} at the same temperature could be used to calculate the percent crystallinity of the polymer or polymer blend:

$$\text{percent crystallinity} = 100(1 - V_g^o/V_g^{o*}) \qquad (61)$$

Courval and Gray[133] indicated that errors in the estimation of polymer crystallinity by IGC could arise from three sources: measurements of GC retention volumes, the uncertainty in the extrapolation used to eliminate surface effects, and errors introduced during extrapolation of amorphous retention data from above T_m to below T_m. They also pointed out that, without correcting for surface adsorption, estimated crystallinity values could vary from 40 to 70%, depending on column loading.[133] They found values of percent crystallinity for poly(oxyethylene)oxide equal to 0.83 ± 0.03 and 0.86 ± 0.05 using retention data for water and *n*-propyl alcohol, respectively.

Chen and Al-Saigh[17] determined the percent of crystallinity for poly(vinylidene fluoride) (PVF2) over the temperature range 80 to 160°C (see Table III in Reference 17). The percent crystallinity was measured for four members of an acetate series and averaged at each temperature. It was found to change from 64.1% at 80°C to 28.7% at 160°C.[17] The error in the averaged crystallinity values was less than 3%.

B. Silicas

The results of experiments carried out at infinite dilution and at finite concentration of the solutes indicated that esterification of silica results in a decrease of surface free energy.[31,32] The adsorption free energy of the solute probes (ΔG°) were higher on precipitated (P) silica than on fumed (A) silica, which was explained by the higher surface hydroxyl group content of the P samples.[31] The grafting of an alkyl chain to the silica caused significant decreases in ΔG°, which was greater for hexadecyl-modified silicas relative to those esterified with methanol. The observed decrease in ΔG° was explained by two types of interactions between the solute and the grafted alkyl chains: (1) adsorption at the gas-grafted chain interface and (2) solvation of the solute by the grafted chains. These observations were confirmed by measurements of the adsorption enthalpies of alkanes on hexadecyl-modified silicas.[31] The ΔH values were almost the same on both silicas and were very close to the heat of dissolution of the probes in hexadecane. The values of the dispersive component of the surface free energy γ_s^d and isosteric heats of adsorption proved that the surface of the initial, uncovered silicas were energetically very heterogeneous, while, upon grafting, their energetic homogeneity greatly increased.[31,32] A decrease in γ_s^d (deactivation of the surface) is enhanced with the increase of the length of grafted alkyl chain (Table 5). Values of γ_s^d for precipitated and fumed silicas grafted with hexadecyl chains are close to the γ_s^d value for polyethylene, which is equal to 35.6.[31,32] Moreover, the very small values obtained for the C_s and C_s' constants (see Equation 41) (which are related to the Lewis acidity and basicity of the surface, respectively), indicated that, after grafting of the hexadecyl chains, the specific component of the surface free energy of silica is strongly reduced.[31,32]

TABLE 5
Values of γ_s^d vs. Temperature for Modified Silicas[31]

Sample	Equation[a]	γ_s^d ± [mJ/m²][b]
Precipitated silica — P	$\gamma_s^d = 106.29 - 0.407 * T$	98.2
P grafted with methanol	$\gamma_s^d = 74.08 - 0.293 * T$	68.2
P grafted with hexadecanol	$\gamma_s^d = 36.75 - 0.058 * T$	35.6
Fumed silica — A	$\gamma_s^d = 81.69 - 0.320 * T$	75.3
A grafted with methanol	$\gamma_s^d = 75.58 - 0.321 * T$	70.2
A grafted with hexadecanol	$\gamma_s^d = 40.56 - 0.096 * T$	38.7

[a] T = temperature (°C).
[b] Value of γ_s^d extrapolated at 20°C.

Similar results were obtained for silicas grafted with poly(ethylene glycols) (PEG).[33] Their properties depended on the surface density of the monomer units. The surface properties of the solid were screened by the increasing coverage of PEG molecules. The dispersive component and the enthalpies of adsorption of different solute probes decreased with the increase of the numeral grafting ratio (n_{MU}) (Table 6). For high surface coverage, ΔH values were comparable to those measured on pure PEG.

Measurements of specific interaction parameters (I_{sp}) for polar solutes showed that increasing the coverage of a very acidic silica surface with PEG chains effected an increase in the predominance of the ether linkages of the polymer. Eventually, it conferred base-like properties to the grafted silica surface.[33]

Comparison of the surface properties of silicas grafted with oligomers or with diols of equal chain length confirmed the importance of the parameter describing the number of monomer units per surface area. The presence of higher numbers of accessible hydroxyl groups resulted in higher values of γ_s^d and enthalpies of adsorption.[33] Substitution of an ethoxylated chain (PEG) by the hydrocarbon chain (diols) increased the interaction energies and the surface acidity. In the case of octanediol and decanediol grafts, London in-

TABLE 6
Dispersive Component of the Surface Energy γ_s^d and Adsorption Enthalpies of Different Probes on PEG-Modified Silicas[33]

		Parameter						
		γ_s^d [mJ/m^2]	ΔH [kJ/mol]					
Sample[a]	n_{MU}	120°C	Heptane	Octane	Nonane	$CHCl_3$	Benzene	Ether
A300/—/0	0	58	55	61	69	43	51	—
A300/2000/5	2.6	31	43	48	54	40	40	55
A300/4000/7	3.6	31	40	45	48	36	37	51
A300/2000/17	8.9	29	36	43	46	37	34	39
A300/2000/23	12.1	31	—	—	—	—	—	—
A300/2000/56	29.5	24	30	36	40	35	28	21
A300/10000/57	30.0	24	32	36	41	37	31	23
A300/4000/72	37.9	24	30	34	39	36	30	28
A300/10000/75	39.5	24	—	—	—	—	—	—
PEG	—	—	27	—	—	37	32	—
ΔH_{vap}	—	—	32	34	37	29	31	29.5

The reference of the sample indicates the silica (Aerosil A300 from Degussa), the molecular weight of the graft, and, in the last row, the grafting ratio (percent).

teraction forces between the hydrocarbon chains are strong enough to promote association. The authors[33] suggested the existence of a "sandwich" structure, in which the hydrocarbon chains are held together by dispersive forces and the terminal hydroxyl groups are associated through H bonds.

Balard et al.[35,37] used IGC to examine the influence of the chain length of grafted *n*-alcohols and α,ω-diols on the surface properties of modified silicas. They found two minima in a plot of γ_s^d vs. number of carbon atoms. These minima correspond to the formation of the first monolayer and the second CH_2 layer on the surface of the silica. The authors suggested that both grafted *n*-alcohols and diols adopt a *trans-trans* layered conformation on the surface of pyrogenic silica.

Ligner et al.[137,138] examined the variation in the dispersive component (γ_s^D) of surface energies[137] and the specific interaction capacity (I_{sp})[138] during and after thermal treatment of silicas. They examined three types of silicas: amorphous, colloidal, and fibrous; and crystalline. The variation of γ_s^D of amorphous silicas upon heating is very complex due to complex chemical changes on the surface of the silicas during the process. The first step is the elimination of physically sorbed water molecules, followed by the thermal condensation of proximal silanol groups. They[137] found the general trend of the curves relating γ_s^D to treatment temperatures to be the same for all examined amorphous silicas. Similar variations in γ_s^D were found for heat-treated fibrous and colloidal silicas. These samples exhibited very high γ_s^D values, about 60 mJ/m^2 higher than the value measured on the other silicas (at maximum point). The variation of γ_s^D in crystalline silicas was quite different from those observed for all other silicas. The authors suggested that physisorbed water is adsorbed less energetically on these samples and leaves the surface after heating at 100°C. Then, a high energetic silica surface is formed on which alkanes strongly adsorb. Ligner et al.[137] indicated that their results support the possibility of the penetration of linear *n*-alkanes inside the lamellar structure of the crystalline silica. However, they also mentioned that such a possibility contradicts the assumptions made in the evaluation of γ_s^D.

The specific interaction capacity of amorphous silicas, expressed as I_{sp} for chloroform, decreases progressively as the heat-treatment temperature increases.[138] This decrease was caused by the elimination of silanol groups. The value of I_{sp} for crystalline silicas increased during the first step of heat treatment due to increasing attraction forces of the polar probe inserted into the silica lamellar layer when the silica interlamellar sheet distance decreases. At higher temperatures, the thermal decomposition of the silanol groups decreases the I_{sp} value. Such conclusions were supported by ^{29}Si CP MAS NMR spectroscopy experiments. The authors[137,138] emphasized the efficiency of inverse gas chromatography as a method for detecting and following molecular changes of the surface of finely divided solids.

Jagiello et al.[139] used inverse gas chromatographic data for the calculation of the adsorption energy distribution function. They described this function as a convenient representation of the interaction ability of the silica surface. This distribution function is sensitive to surface changes caused by physical or chemical modification (thermal treatment, grafting).

C. Other Materials

IGC was also used to examine other materials, such as calcite,[36] mica,[140] egg powders,[56] heavy oil residues,[55] and petroleum pitches.[53] Schmitt et al.[36] compared the properties of untreated calcium carbonate with $CaCO_3$ treated with stearic acid. They observed that the adsorption enthalpies of *n*-alkanes as solute probes measured on treated $CaCO_3$ were significantly higher than those for untreated calcite, and were close to the condensation enthalpies of *n*-alkanes. The authors[36] attributed this effect to the different retention mechanisms. In the case of untreated $CaCO_3$, the process is controlled by gas-solid adsorption. On modified $CaCO_3$, the possible alkanes dissolve between the grafted hydrocarbon chains. These observations were supported by values obtained for the dispersive component of the surface energy γ_s^d.[36] These results were similar to those described above for grafted silicas.[31-35] The modified material progressively changed its properties and at sufficiently high surface coverage its characteristics depended mainly on the chemistry of the modifying agent.

Papirer et al.[140] reported significant changes in the dispersive component of the surface energy and specific energies of interactions for mica samples treated with toluene, methanol, and water. The properties (γ_s^d) of treated mica depended on the time of the modification process and were influenced by the degree of change in its specific area. Upon grinding, the surface properties of all samples were altered. Their base-like properties increased while acid-like ones slightly decreased.

Demertzis and Kontominas[57] studied water absorption on vinylidene chloride/vinyl chloride and vinylidene chloride/acrylonitryle copolymers. These workers suggested that relatively high values of ΔH_{ads} (-10.0 kcal/mol) corresponded to very strong polymer/water interactions and supported the active-site hypothesis.

Papirer et al.[55] characterized the surface properties of heavy residues of oil distillation (i.e., asphalt and asphaltenes), which are complex colloidal systems. A silica support was carefully deactivated and then impregnated with the heavy residues. Surface properties were characterized by evaluating the dispersive component of the surface energy (Equation 39) and the specific component of the surface energy (Equation 41). The dispersive component of the surface energy of the examined materials decreased with increasing temperature of the experiment. The γ_s^d values for asphaltene were higher than the corresponding values for asphalt. The authors indicated that it is possible in asphalt (a mixture of asphaltenes and resins) that polar groups responsible for the high γ_s^d values partially neutralize each other. They also found that asphaltenes possessed pronounced acid/base characteristics, i.e., higher C_s and C_s' values in Equation 41 (see Table IV in Reference 55).

D. Fibers

Saint Flour and Papirer[136,141] characterized glass fibers in terms of specific interactions between a testing solute and the examined fiber material. Untreated, silane-treated, and titanate-treated glass fibers were characterized by determining $\log_{10}\frac{V_{g\ \text{benzene}}}{V_{g\ \text{hexane}}}$ and $\log_{10}\frac{V_{g\ \text{ether}}}{V_{g\ \text{pentane}}}$ values, as well as by rearranging Equation 41. The authors used Equation 41 in the form

$$I^{ab} = C_aC_b + E_aE_b \qquad (62)$$

where I^{ab} is the difference in $\log_{10}V_g/V_g^*$ between a given solute and the corresponding *n*-alkane of equal vapor pressure; and C_a, C_b, E_a, and E_b have the same meaning as in Equation 27.

All the results presented indicated that silane-treated glass surfaces are poorer electron acceptors than untreated surfaces. Titanate treatment enhanced the affinity of the glass surface for electron donors. The authors explained the properties of the examined materials on the basis of the structure of the surface layers.[140] The relatively thick silane layer (not completely cross-linked, with isolated amino groups outside of the layer and variation in composition with thickness) caused a poorer electron acceptance than untreated surfaces. Titanate treatment enhanced the affinity of the glass surface for electron donors. The authors explained the properties of the examined materials on the basis of the structure of the surface layers.[140] The relatively thick silane layer (not completely cross-linked, with isolated amino groups outside of the layer and variation in composition with thickness) caused a poorer electron acceptance of silane-treated fibers. Titanates form a monolayer of a coupling agent on the solid surface, and the appearance of hydroxyl groups linked to the titanium atoms during treatment is also possible. These groups are acidic and cause an enhanced affinity for electron donors.

These results were related to the mechanical properties of glass fibers/phenolic resins composites. Since phenolic resin exhibits acidic behavior, it will bind preferentially with the more base-like surface of the silane-treated glass fiber than with the untreated fiber.

Grenier-Loustalot et al.[29] examined the properties of carbon fibers oxidized and sized with polyesters. They characterized these materials by determining the partition coefficient K° (Equations 31 to 32) for different organic solutes (dodecane, butylbenzene, pentanol) and water. The authors found IGC to be useful for quantifying the affinity of fibers for organic compounds.

Nardin et al.[143] studied the surface characteristics of carbonized and stabilized carbon fibers. They determined the dispersive component of the surface energy and, by using polar probes, the acid-base surface characteristics for both types of fibers. Carbonized fibers present an electron-donating or base character, suitable for strong interactions with an acidic resin. Stabilized fibers were more amphoteric and will interact with any resin.

E. Surfactants and Extractants

A number of members of this large group of surface-active compounds and extractants have been examined by the IGC method. These materials, in most cases, are classified according to polarity, which in turn determines their behavior at the oil/water interface. The influence of the structure of nonionic oligooxyethylene surface-active agents was extensively examined in a series of papers.[42-51,101-104] It was found that the polarity of a compound A_i (P_{Ai}) can be expressed as

$$P_{Ai} = \text{constant} + \Sigma\, a_{ji}\Delta P_{Gj} \qquad (63)$$

where it is assumed that the increment of ΔP for group G_j is constant for all compounds present in the system, and the coefficient a_{ji} denotes the number of G_j groups in compound A_j.[5,144,145]

The increments obtained for different homologous series were used to predict the polarity parameters for the considered compounds and their homologs from their formulae. The relative polarities of different structural increments were determined as follows: –OH > –N< > –NH– > –Cl > –O– > –S–. They depend upon the type of the compound and the polarity parameter considered; however, this sequence remains generally valid.[144,145]

The properly chosen polarity parameter should entirely reflect the energy of interaction between the standard solute and the examined stationary phase (surfactant). Any change in the structure of the liquid phase should be accompanied by a change in the considered polarity parameter. The polarity parameters used in experiments with surfactants and extractants as liquid phases exhibit different sensitivities depending upon structural differences in the liquid phases.[46,50,144] The sensitivity of a given polarity parameter was quantified as $[(P_{max} - P_{min})/P_{min}]*100\%$, where P_{max} and P_{min} are its maximal and minimal values for an examined group of compounds (Table 7). The most sensitive parameters seem to be coefficient ρ and the sum of the first five McReynolds' constants $\Sigma_{i=1}^{5} \Delta I_i$. The thermodynamic parameters, such as the partial molal Gibbs free energy of solution for the methylene group $\Delta G_s^m(CH_2)$ or criterion A, are much less sensitive to structural changes in the liquid

TABLE 7

Sensitivity of Polarity Parameters $\frac{P_{max} - P_{min}}{P_{min}}$ * 100%[145]

	Polar Probe	A	B	C	D	E	F	G
		Group of Compounds — Stationary Phase						
I_R	Methanol	74	27	22	35	42	20	79
	Ethanol	75	23	18	28	56	20	—
PI	Methanol	165	87	35	79	34	38	117
	Ethanol	120	44	25	48	27	29	—
ρ	Methanol	1957	198	224	393	225	171	356
	Ethanol	1162	184	191	292	416	171	—
ΔG_s^m (OH)	Methanol	76	—	16	23	28	30	—
	Ethanol	91	—	20	25	32	21	—
ΔG_s^m (C=O)	2-Butanone	105	—	—	—	31	23	—
	2-Pentanon	160	—	14	22	25	22	—
$\Sigma_{i=1}^{5} \Delta I_i$	—	331	—	62	128	172	67	—
Criter. A	Alkanes	24	—	8	17	—	—	10
ΔG_s^m (CH_2)	Alkanes	37	—	8	13	—	—	—
ΔG^E (CH_2)	Alkanes	86	—	55	109	—	—	43

* A = oligocxyethylene derivatives of alcohols, thioalcohols, and alkylamines
B = polyoxyethylene dialkyl ethers and their sulfur analogs
C = di- and trialkyl ethers of aminoeteroalkanols
D = 1,3-bis-[ω-alkoxyoligo(oxyethylene)]-propan-2-ols
E = alkyl derivatives of α,ω-diaminooligoethers
F = alkyl derivatives of diazaoligooxyethylene ethers
G = aromatic hydroxyoximes and their intermediates

phase. They should be used only in this case when a satisfactory precision of their determination is assured. The sensitivity of the partial molar excess Gibbs free energy of solution per methylene group $\Delta G^E(CH_2)$ is much higher and is comparable to that of $\Sigma_{i=1}^{5} \Delta I_i$ or the polarity index PI. Szymanowski, in his review, has pointed out that empirical polarity parameters, the retention index of alcohol I_R, and the polarity index PI can be precisely determined in standard experiments.[51] They are sufficiently sensitive to be used to study the effects of structural changes in the surfactants' molecules on their polarities and surface-active properties. Szymanowski extensively discussed the use of polarity parameters in assessing the behavior of extractants and surfactants at liquid/liquid interfaces.[51] They also have been used to evaluate kinetic data and the mechanism of metal extraction by various extractants.

V. CONCLUDING REMARKS

Inverse gas chromatography has been widely used in the characterization of the physicochemical properties of a variety of materials. Its sensitivity to very small differences in the structural composition of examined substances has been established. Almost all reports have addressed the mixed retention mechanism. Many authors have described procedures that have been established to eliminate or correct for adsorption effects at gas-support and gas-liquid interfaces, and the influence of the flow rate of carrier gas on the measured retention data. However, these procedures could produce another source of error. For example, the procedure proposed for the elimination of the influence of the support does not take into account the area occupied by the liquid phase. Also, there is no theoretical background for an extrapolation to zero flow rate to eliminate the effect of the carrier on the solute-specific retention volume. In addition, very often the net retention volume has been used instead of the specific retention volume, and/or the retention volume was not converted to 273.15 K as a standardization condition.

Papirer et al. used adsorption parameters for evaluation of the properties of modified silicas.

However, even in this case, some effects could be explained only by solution of the solute probe in the hydrocarbon chain grafted on the solid surface of the silicas.

Flory-Huggins theory, thermodynamic parameters, and polarity parameters were derived under the assumption that the partition process is the prevailing process during solute retention interactions. Consequently, most efforts were directed to "extract" that part of the solute retention volume due to the partition process. As we have seen, the involved procedures are not free of errors. A procedure described by Poole et al.[62,66-70] and others[90-92] involved the usage of separated partition coefficients for both types of interactions. Unfortunately, this procedure requires the redefinition of basic equations in terms of K_L or K_A, instead of V_g.

However, the examined materials behave during the technological retention process in a manner determined by the complex properties of their surface and/or bulk liquid. Their behavior is simultaneously influenced by the amount of the molecules (surfaces) involved in the sorption and adsorption interactions. The question is, do the parameters that have been derived fully describe the activity of examined materials in the technological process? It seems that, so far, since we cannot define appropriate parameters that fully describe the very complex nature of the materials, we should use the existing parameters. However, we must remember that the obtained parameters are significantly limited.

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