

Acid–Base Interactions in Filler Characterization by Inverse Gas Chromatography

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SYNOPSIS

Glass beads as model fillers were characterized by inverse gas chromatography (IGC) according to the Lewis acid–Lewis base (donor–acceptor) concepts as adapted by Fowkes. A range of organic probes (acidic chloromethanes, neutral *n*-alkanes, and basic acetone and diethylether) was used to elucidate the acid–base nature of the glass bead surface. The untreated glass bead surface was found to contain predominantly acidic sites while the treated glass bead (treated with an aminopropyltriethoxysilane coupling agent) was more basic than its unmodified counterpart. Calculation of the enthalpies of acid–base interactions (ΔH^{ab}) from the retention behavior of the basic probes with the two glass beads produced at least an 8-kJ/mol difference between the two glass types, the ΔH^{ab} of the untreated glass being greater than the treated glass. A difference of this magnitude is sufficient to produce a corresponding difference in the interfacial behavior of the two glass types. Therefore, IGC can be used as a quantitative technique for characterizing filler surfaces.

INTRODUCTION

The increasing use of polymer composites has stressed the importance of characterizing filler surfaces to understand their adsorption behavior with polymeric materials. Recently, inverse gas chromatography (IGC) was used to evaluate fillers and polymeric materials according to the Lewis acid–Lewis base (donor–acceptor) theories of Drago as adapted by Fowkes for liquid–solid, liquid–liquid, and solid–solid interactions.^{1–11} The phrase “inverse gas chromatography” was introduced to denote that the component of interest is the stationary phase, which may be filler or polymeric material.¹² Except for the role reversal of the solute probe and packing material, the principle and instrumentation behind IGC are identical to that of gas chromatography (GC). For GC, the packing material, which is well characterized in most cases, serves to separate or identify the various components of an unknown. In

contrast, IGC utilizes specific solute probes to elucidate the interaction behavior of the packing material. For this reason, IGC is an ideal method for characterizing materials.

This investigation utilized IGC as an analytical technique for characterizing material surfaces and developed an approach to quantify the adsorption behavior of materials. Spherical glass beads as model fillers (untreated and treated with an aminopropyltriethoxysilane) were packed directly into the GC column as the stationary solid phase. More importantly, the acid–base characteristic of the glass filler surface was determined by utilizing low molecular weight organic probes or adsorbates whose acid–base behaviors are well established. The underlying assumption of this method is that infinite dilution may be obtained by injecting small amounts of probes in the vapor form.

The data will demonstrate the relationship between the trends in net retention times (t_N) and the donor–acceptor character of the filler surface. Second, calculation of the heats of adsorption (ΔH_A) of the various adsorbates will illustrate that the IGC method can provide a quantitative measure of the acid–base strength of the material. In this case, it is important to establish firmly that ΔH_A equals ΔH^d

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(heats of adsorption due to dispersion interactions) for neutral probes. Correspondingly, for probes that can undergo specific interactions, it is important to show that ΔH_A is the summation of ΔH^d and ΔH^{ab} (heat of adsorption due to acid/base interaction).

In addition, the glass beads were examined by X-ray photoelectron spectroscopy (XPS) to confirm the presence of the aminosilane coupling agent.

Measurement of Heats of Adsorption (ΔH_A)

From classical chromatography, the following expression holds:

$$V_N = k \{ \exp - [\Delta H_A / R * T] \} \quad (1)$$

where V_N corresponds to the net retention volume of the solute probe, R is the gas constant, T is the temperature of measurement in K , and ΔH_A is the partial molar enthalpy of adsorption at zero coverage of the adsorbate.¹³⁻¹⁵ Equation (1) is a van't Hoff relationship that calculates the ΔH_A at effectively zero surface coverage provided that the following conditions are met: gas-phase ideality holds, the adsorption of the probe at the gas-solid interface governs the retention mechanism, and Henry's law applies.¹⁴⁻¹⁷

For a pure solute, ΔH_A constitutes a combination of several intermolecular interactions: dispersion forces, dipole-dipole or polar interactions, acid-base interactions, etc. In earlier work, Fowkes and Mostafa demonstrated that the contributions of dipole-dipole and other interaction terms are negligible in comparison to those due to dispersion and acid-base interactions.¹⁸ More importantly, in theory, ΔH^{ab} is equivalent to the enthalpy of hydrogen bonding as proposed by Drago and Wayland and Drago et al. for calculating the degree of interaction between a donor-acceptor pair.^{19,20}

In general, there are three contributions to the adsorption process for gas-liquid chromatography: partitioning of the probe with the liquid phase, adsorption of the probe at the gas-liquid interface, and adsorption of the probe at the surface of the solid support.²¹ For gas-solid chromatography, particularly for glass beads, gas adsorption is the primary retention mechanism, though the probe may be retained by bulk sorption and/or adsorption in the underlying support of a treated glass. This slow bulk sorption may cause spreading and distortion of the GC measurements, producing unreliable results.^{10,21-24}

A number of methodologies have been introduced to obtain infinite dilution bulk retention volumes

from asymmetric peaks for multiple sorption mechanisms.^{11,13,22,25-27} Chamberlain and Drago applied the Liao and Martire approach to calculate the enthalpies of acid-base interactions.^{28,29} The enthalpies of hydrogen bonding obtained by GLC were in good agreement with those calculated by calorimetry (which is the conventional method of enthalpy determination) and infrared frequency shifts, indicating that the GLC method is a quantitative method for obtaining heats of adsorption.²⁸ Equally important, the heats of adsorption predicted by the Drago equation using the Drago parameters correlated with the values obtained by the three methods. The important point to stress is that the various approaches have been shown to calculate the heats of adsorption of the probes with the column packing.

Several investigators have made IGC measurements to determine the Flory-Huggins interaction parameter for various solutes.^{16,30-32} Of more interest to this work, Anhang and Gray applied Eq. (1) to directly measure ΔH_A at effectively zero coverage,¹⁵ which is more compatible with the acid-base approach.

For a neutral adsorbate/substrate combination, ΔH_A of the solute will be due predominantly to dispersion interactions when surface adsorption is the dominant retention mechanism. Therefore, ΔH_A equals ΔH^d and is close to ΔH_{vap} .^{15,33} These findings confirm the absence of acid-base effects for neutral adsorbates and reaffirm the applicability of Eq. (1). Whether the actual value is less than or greater than ΔH_{vap} depends on the absence or presence of high-energy sites on the filler surface, which do not possess donor-acceptor characteristics because the adsorption of neutral adsorbates such as n -alkanes are affected by them. Surface heterogeneity appears to be the general rule as opposed to surface homogeneity, particularly for surfaces that might contain residues.^{13,15,16}

Overall, the treatment of a neutral probe is relatively straightforward because dispersion forces are the principal mode of interaction. At zero surface coverage, the gas chromatogram's peak maximum (which is expected to be symmetrical) is the retention time of the probe.^{15,34,35}

Determination of ΔH^{ab}

An important fundamental and theoretical question involves the measurement of ΔH_A of an acidic (basic) probe with a basic (acidic) substrate. In principle, gas chromatography requires the use of quickly eluted adsorbates.¹³ However, the greater the acid-base interaction between the adsorbate and sub-

strate, the more the resulting isotherm deviates from ideality. The analysis of an asymmetrical isotherm is often much more difficult and the interpretation may be subject to theoretical arguments. Peak shape depends on one or a combination of factors, but in theory, a nearly symmetrical peak is obtainable when the solution is at infinite dilution or zero surface coverage.¹³

One approach for characterizing materials involves the careful selection of a series of probes that span the range of donor-acceptor behavior; i.e., from basic to neutral to acidic. Comparison of the net retention times of the various solutes provides a measure of the relative acid-base strength of the substrate. An estimate of ΔH^{ab} is possible by subtracting the heat of vaporization (ΔH_{vap}) of the adsorbate from the experimentally determined ΔH_A ; the greater the difference between the two values, the stronger the acid-base interaction. Thus,

$$\Delta H^{ab} \simeq \Delta H_A - \Delta H_{vap} \quad (2)$$

This approach assumes that ΔH_{vap} provides a good estimate of ΔH^d . However, for adsorbates capable of self-association, ΔH_{vap} is not solely attributable to dispersion-type interactions, and use of Eq. (2) will overestimate ΔH^d . Other expressions may be used to estimate ΔH_{vap} , i.e., Trouton's rule³⁶ and Riedel's equation.^{37,38}

Another approach effectively separates the dispersion component by subtracting the ΔH_A of a neutral model compound of approximately the same size. A relation developed by Arnett et al. may be modified to obtain ΔH^{ab} from experimental values of ΔH , ΔH_{exp} .³⁹

$$\Delta H^{ab} = (\Delta H_{exp} - \Delta H^d)_{probe} - (\Delta H_{exp} - \Delta H^d)_{model} \quad (3)$$

In this case, the model probe must be neutral and approximately similar in size to the adsorbate probe.^{2,3} Clearly, the key in obtaining a good value of ΔH^{ab} resides in the approximation of the ΔH^d and must take into consideration the assumptions made in the derivation of the particular expression.

Other investigators have developed terms or measured the heats of interaction of a variety of materials to quantify their adsorption behavior. Schreiber introduced the Ω interaction parameter.^{4,9,10} Saint Flour and Papirer utilized a number of approaches to evaluate the donor-acceptor behavior of glass fibers,^{7,8,40,41} including the concept of donor numbers as proposed by Gutman.⁸ In addition, Braun and Guillet have studied the adsorption be-

havior of polymers using fundamental principles.⁴² Also, the contributions of Smidsrod and Guillet on the use of GC to investigate polymer-solute adsorption should be mentioned because their work stimulated numerous investigations on the subject.⁴³ Finally, other investigators have reported the effects of experimental variables at the polymer glass transition region.⁴⁴⁻⁵⁰

EXPERIMENTAL

Inverse Gas Chromatography

Equipment

A Perkin-Elmer Sigma 3 gas chromatograph with a flame ionization detector (FID) was used for the IGC measurements. Injection block and detector cell temperatures were controlled by the instrument, with cell temperature at 180°C for all measurements. The Sigma 3 unit was capable of maintaining the oven compartment to $\pm 0.2^\circ\text{C}$. The helium carrier gas flow rate was controlled by the instrument at 30 mL/min and checked by a soap bubble technique.

The glass beads designated as type 3000 (untreated) and 3000CP03 (treated with an aminopropyltriethoxysilane) were supplied by Potters Industries and were reported to have the following bulk composition: $\text{SiO}_2 = 72.5\%$, $\text{Na}_2\text{O} = 13.7\%$, $\text{CaO} = 9.8\%$, $\text{MgO} = 3.3\%$, $\text{Al}_2\text{O}_3 = 0.4\%$, FeO and $\text{Fe}_2\text{O}_3 = 0.2$, and $\text{K}_2\text{O} = 0.1\%$. The glass beads had a mean particle size of $\sim 25 \mu\text{m}$ and an average specific area of $1.2 \text{ m}^2/\text{g}$. Approximately 38 g of the unmodified and treated glass were packed in premium-grade stainless steel tubes (1.22 m long and 6.35 mm in external diameter) into separate columns using a mechanical vibrator.

Probe Molecules

The adsorbates were analytical grade of low water content; *n*-heptane and *n*-octane (Sigma Chemical Co., < 1%), CH_2Cl_2 and CHCl_3 (Fisher Scientific, < 0.02%), acetone (Fisher Scientific, < 0.5%), *n*-pentane (Fisher Scientific, < 0.5%), and laboratory grade diethylether (Fisher Scientific). The adsorbates were used as received without further purification. A small portion of the liquid adsorbate was poured into 50-mL glass vials containing Fischer Scientific 4A molecular sieves to remove residual water and encapsulated with rubber septums. The vials were stored in a desiccator and allowed to dry overnight over the molecular sieves prior to use. Ex-

cept for the brief period before injection of the probe, the vials remained in the dessicator.

CHCl_3 and CH_2Cl_2 were selected as the acidic probes while acetone and diethylether served as the basic probes. The neutral probes included carbon tetrachloride, *n*-pentane, *n*-heptane, and *n*-octane.

IGC Measurements

Before each series of measurements, the column was conditioned at 120°C for at least 12 h under dry flowing helium gas. A Hamilton 10-mL gas-tight syringe with a Teflon-tip plunger was used to introduce less than 0.1 mL of adsorbate vapor into the column. In addition, the septum at the injection port was replaced periodically to prevent backflow of carrier gas or sample. Furthermore, the FID was optimized and cleaned periodically to ensure operation at the highest sensitivity possible.

For the chloromethanes and neutral adsorbates whose isotherms were predominantly symmetrical, the retention times (t_R) were calculated from the peak maxima. The chloromethanes showed a slightly skewed isotherm, but the maximum peak height was not concentration dependent. However, for ether and acetone, t_R was computed from the point where the sample chromatogram initially deviated from the base line. Since the t_R of the basic adsorbates were skewed and showed strong dependence with concentration, only those isotherms exhibiting the lowest concentration were selected to represent t_R at the specified temperature. The minimum concentration was defined as 1% of the maximum peak height resulting from the injection of < 0.1 mL vapor of solute.

Measurements were made, at least in duplicate, for the chloromethanes and neutral probes from 40 to 100°C . t_R values for the basic probes, whose retention times were much longer, were determined at higher temperatures, 100 – 160°C . After each run, sufficient time was allowed to elapse before the next probe injection to ensure the removal of residual adsorbates on the substrate surface.

Finally, t_N was calculated by subtracting t_R from the retention time of methane. For the same GC column and under identical experimental conditions, t_N accurately reflects the magnitude of the net retention volume of different adsorbates.

X-Ray Photoelectron Spectroscopy

A Physical Electronics Model 548 XPS/Auger spectrometer was utilized to analyze the glass surface while micrographs of the fillers were made possible

by an ETEC scanning electron microscope (SEM) unit.

RESULTS

Surface Analysis

SEM micrographs and XPS analysis revealed differences in the surfaces of the two types of glass. Figure 1 shows the surface of the treated glass spheres to be rougher in appearance than those of the untreated ones, while XPS studies indicated the presence of elemental nitrogen on the treated glass but not on the untreated ones, confirming the presence of the amino groups on the treated glass surface.

Filler Characterization by IGC

Table I illustrates the Lewis acid–base order of the various adsorbates, and their corresponding Drago *E* and *C* parameters. For the acidic and basic probes, the selection of a neutral probe approximately similar in size helps to elucidate the contribution of the dispersion component from the overall adsorption interactions. Carbon tetrachloride represents the neutral adsorbate in the family of electron-accepting chloromethanes, while *n*-pentane provides a similar role for the oxygen-containing electron donors. Correspondingly, the ability of IGC to differentiate between two homologous *n*-alkanes (*n*-heptane and *n*-octane) will establish the sensitivity of the IGC technique.

An important assumption of the IGC measurements in the vapor phase is that gas adsorption is the predominant retention mechanism. This is so because the low solute probe concentration produces a condition in which a very thin layer of probe molecules are adsorbing onto a high surface-to-volume-ratio filler. In a rigorous manner, this assumption

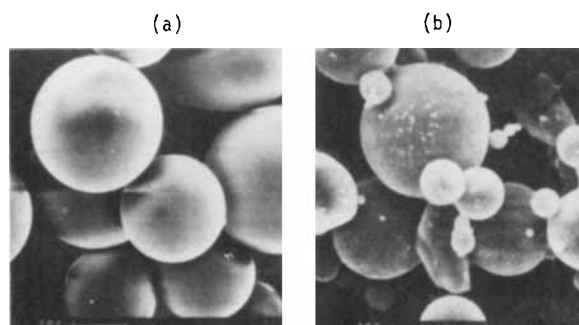


Figure 1 Scanning electron micrographs of glass spheres: (a) untreated, (b) treated with an aminosilane.

Table I Drago Parameters^a for the IGC Probes

	Probe	C_A	E_A	C_B	E_B
Acidic	CHCl ₃	3.31	0.15	—	—
	CH ₂ Cl ₂	1.66	0.01	—	—
Basic	Dimethylketone	—	—	2.33	0.987
	Diethylether	—	—	3.25	0.963

^a Drago parameters for the chloromethanes and oxygen-containing probes were obtained from Refs. 20 and 51, respectively. Each parameter has units of (kcal/mol)^{1/2}, and the subscripts *A* and *B* correspond to acidic and basic, respectively.

is justifiable for the unmodified glass but not the treated glass because it is possible for the probe to undergo bulk sorption due to dissolution in the coupling agent or adsorption onto unreacted sites on the silica.⁵²

One other point to address is the question of surface coverage. Ideally, the measurements should be made at monolayer coverage. Calculation of the moles of injected probe per surface area of glass is possible assuming ideal gas conditions at standard temperature and pressure. Using the maximum sample size of 0.1 mL vapor and 1.2 m²/g as the average geometric surface area of glass, the computation yields a value of 1×10^{-6} mol/m². Since monolayer coverage of *n*-hexane and *n*-decane for "hard spheres" has been reported to be 1.2×10^{-6} and 2.5×10^{-6} mol/m², respectively, it is appropriate to assume that the IGC measurements of the

various probes were made at *monolayer coverage*.^{15,53} Therefore, under these experimental conditions, surface adsorption is the dominant retention mechanism.

Figures 2 through 7 graphically illustrate the temperature dependence of the net retention times of the various adsorbates from Tables II through V for both glass types while Table VI summarizes their ΔH_A as calculated by Eq. (1). In addition, Table VII exhibits the ΔH^{ab} computed from various methods of estimating ΔH^d .

From Figures 2 and 5, the net retention times of the neutral probes increase according to the same order for both filler types; *n*-pentane < *n*-heptane < *n*-octane. The net retention times can clearly discriminate between the *n*-alkanes (especially between *n*-heptane and *n*-octane). As expected, the *higher n*-alkane results in *greater* net retention times, and the order parallels the increase in the experimental ΔH_A and ΔH_{vap} values in Table VI,

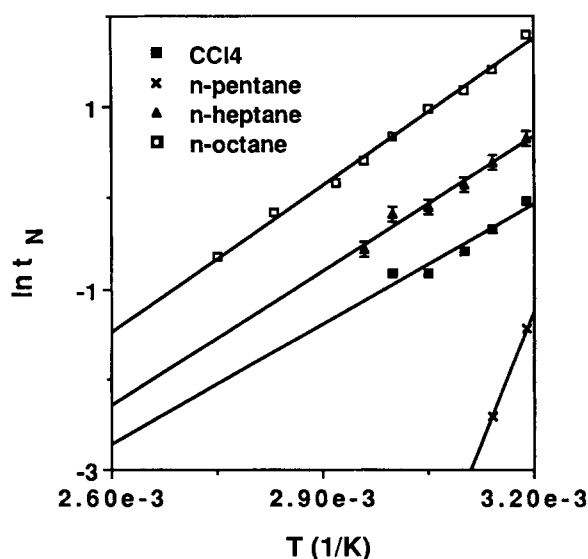


Figure 2 Retention behavior of the neutral probes with the treated glass bead: (×) *n*-pentane, (▲) *n*-heptane, (□) *n*-octane, (■) CCl₄. The error bar for each point corresponds to the maximum error range for each data set.

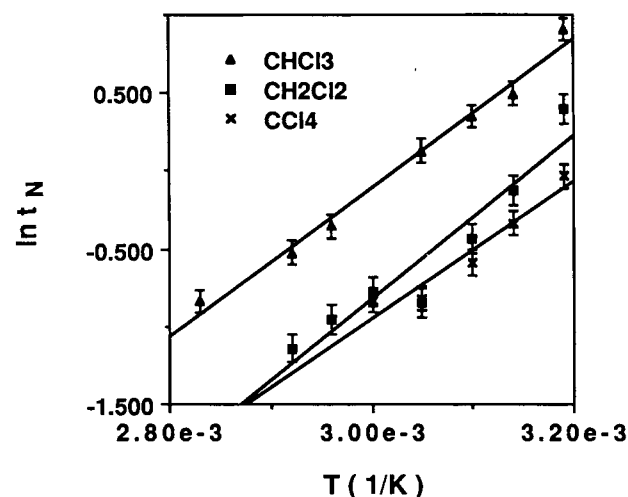


Figure 3 Retention behavior of the acidic probes with the treated glass bead: (×) CCl₄, (■) CH₂Cl₂, (▲) CHCl₃. The error bar for each point corresponds to the maximum error range for each data set.

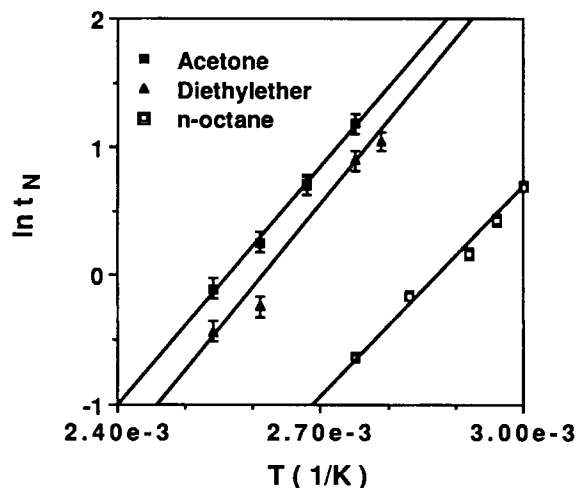


Figure 4 Retention behavior of the basic probes with the treated glass beads: (■) acetone, (▲) diethylether, (□) *n*-octane. The error bar for each point corresponds to the maximum error range for each data set.

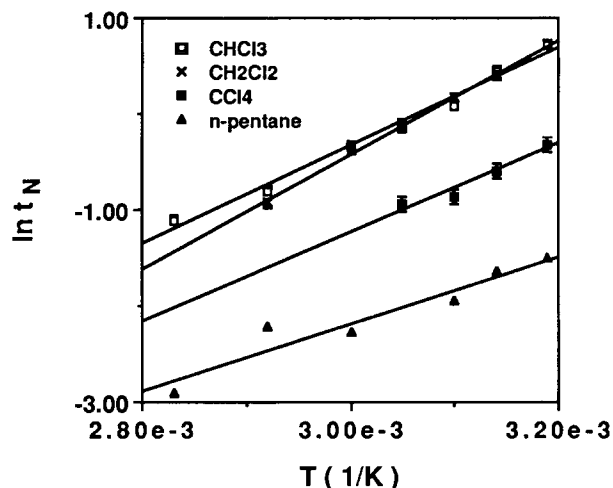


Figure 6 Retention behavior of the acidic probes with the untreated glass bead: (■) CCl_4 ; (×) CH_2Cl_2 , (□) CHCl_3 , (▲) *n*-pentane. The error bar for each point corresponds to the maximum error range for each data set.

particularly for *n*-heptane and *n*-octane. In this case, the adsorption process is predominantly due to dispersion interactions, with ΔH_A slightly greater than the adsorbate heats of vaporization. Moreover, the ΔH_A values in Table VI can distinguish between *n*-heptane and *n*-octane, though the difference is almost within experimental error.

Correspondingly, *n*-pentane exhibits net retention times less than *n*-heptane and *n*-octane but greater than methane. However, the difference between the *n*-pentane peak and the reference meth-

ane peak is small, 11 s at 40°C (the lowest operating temperature of the GC). These observations reflect the chemical composition of *n*-pentane (which is only a methylene group higher than *n*-butane gas) and the operating experimental temperatures (which are evidently too high to provide sufficiently long retention times for *n*-pentane).

The results from the neutral probes (*n*-heptane and *n*-octane) provide the fundamental basis of our experimental approach. From Table VI, each of the neutral adsorbates exhibit ΔH_A values slightly

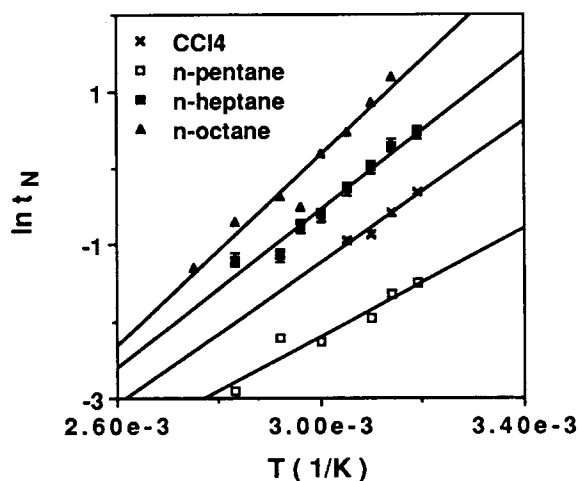


Figure 5 Retention behavior of neutral probes with the untreated glass bead: (□) *n*-pentane, (■) *n*-heptane, (▲) *n*-octane; (×) CCl_4 . The error bars correspond to the maximum error range for each data set.

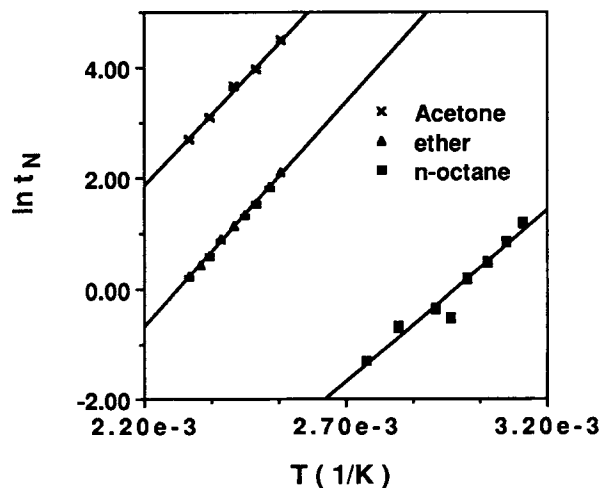


Figure 7 Retention behavior of basic probes with the untreated glass bead: (×) acetone, (▲) diethylether, (■) *n*-octane. The error bar for each point corresponds to the maximum error range for each data set.

Table II Net Retention Times (t_N) of the IGC Probes for the Untreated Glass Bead

T (°C) ($1/K \times 10^3$)	t_N (min)		
	Neutral Probes		
	<i>n</i> -Pentane	<i>n</i> -Heptane	<i>n</i> -Octane
40 (3.19)	0.23 ± 0.03	1.59 ± 0.02	—
45 (3.14)	0.18 ± 0.01	1.33 ± 0.03	3.29 ± 0.05
50 (3.10)	0.15 ± 0.01	1.01 ± 0.02	2.36 ± 0.08
55 (3.05)	—	0.76 ± 0.06	1.62 ± 0.04
60 (3.00)	0.11 ± 0.01	0.54 ± 0.03	1.20 ± 0.04
65 (2.96)		0.47 ± 0.02	0.60 ± 0.01
70 (2.92)		0.32 ± 0.02	0.70 ± 0.01
80 (2.83)		0.30 ± 0.01	0.50 ± 0.01
90 (2.75)			0.27 ± 0.01
100 (2.68)			0.28 ± 0.01

T (°C) ($1/K \times 10^3$)	Neutral Probe CCl ₄	Acidic Probes	
		CH ₂ Cl ₂	CHCl ₃
	40 (3.19)	0.73 ± 0.03	—
45 (3.14)	0.55 ± 0.01	1.49 ± 0.07	1.05 ± 0.04
50 (3.10)	0.41 ± 0.02	1.18 ± 0.06	1.09 ± 0.05
55 (3.05)	0.39 ± 0.01	0.87 ± 0.03	0.90 ± 0.01
60 (3.00)		0.68 ± 0.02	0.71 ± 0.03
65 (2.96)		0.40 ± 0.01	—
70 (2.92)			0.45 ± 0.01
80 (2.83)			0.33 ± 0.01

greater than their heats of vaporization, establishing that the dispersion component of ΔH_A is close to ΔH_{vap} in the absence of specific effects. Also, the difference between the ΔH_A values obtained from the two glass types are well within experimental er-

Table III Net Retention Times (t_N) of the Basic IGC Probes for the Untreated Glass Bead

T (°C) ($1/K \times 10^3$)	t_N (min)	
	Dimethyl Ketone	Diethylether
120 (2.54)	88.8	8.17 ± 0.01
125 (2.51)	—	6.18 ± 0.01
130 (2.48)	52.8	4.72 ± 0.15
135 (2.45)	—	3.74 ± 0.01
140 (2.42)	38.4	3.08 ± 0.04
145 (2.39)	—	2.43 ± 0.04
150 (2.36)	22.3	1.84 ± 0.04
155 (2.34)	—	1.54 ± 0.44
160 (2.31)	14.9	1.27 ± 0.03

ror. This is expected because the acid-base character of the filler surface will not significantly affect the adsorption behavior of a neutral molecule.^{15,34} These findings are strong evidence that the experimental procedure provides quantitative data, at least for neutral adsorbates.

Comparison of the retention behavior and ΔH_A of the acidic and basic probes for each filler type characterizes their surfaces. Qualitatively, it is evident from Figures 3 and 4 and 6 and 7 that the untreated glass possesses predominantly acidic sites, while the treated filler acts as an electron donor relative to the unmodified glass. Quantitatively, the ΔH^{ab} values in Table VII support the general observation that the untreated glass is more acidic than the treated glass.

Comparison of the various methods of predicting ΔH_{vap} (Table VII) attests to the utility of ΔH_{vap} in estimating ΔH^{d} . The order is $\Delta H_A^{\text{Riedel}} < \Delta H_A^{\text{Trouton}} < \Delta H_{\text{vap}}^{\text{CRC}}$.⁵⁴ The fact that ΔH_{vap} exhibits values close to Trouton's rule implies that the chloromethanes and oxygen-containing adsorbates possess a low degree of self-association. In this regard, the choice of

Table IV Net Retention Times of the IGC Probes for the Treated Glass Bead

T (°C) ($1/K \times 10^3$)	t_N (min)		
	Neutral Probes		
	<i>n</i> -Pentane	<i>n</i> -Heptane	<i>n</i> -Octane
40 (3.19)	0.24 ± 0.01	1.94 ± 0.04	6.05 ± 0.16
45 (3.14)	0.09	1.49 ± 0.03	4.13 ± 0.06
50 (3.10)	0	1.17 ± 0.01	3.26 ± 0.05
55 (3.05)	—	0.91 ± 0.01	2.68 ± 0.01
60 (3.00)	0	0.84 ± 0.01	1.99 ± 0.02
65 (2.96)		0.57 ± 0.02	1.53 ± 0.04
70 (2.92)			1.18 ± 0.04
75 (2.87)			0.85 ± 0.01

T (°C) ($1/K \times 10^3$)	Acidic Probes		
	Neutral Probe CCl_4	CH_2Cl_2	CHCl_3
	40 (3.19)	0.97 ± 0.01	1.49 ± 0.01
45 (3.14)	0.72 ± 0.05	0.88 ± 0.01	1.64 ± 0.12
50 (3.10)	0.58 ± 0.04	0.65 ± 0.01	1.42 ± 0.05
55 (3.05)	0.44 ± 0.01	0.43 ± 0.07	1.14 ± 0.03
60 (3.00)	0.44 ± 0.01	0.46 ± 0.03	—
65 (2.96)		0.39 ± 0.01	0.70 ± 0.02
70 (2.92)		0.32 ± 0.02	0.59 ± 0.05
75 (2.87)			—
80 (2.83)			0.43 ± 0.03

probes is appropriate because adsorbate–adsorbate interactions are minimal and will not contribute to nonideal behavior. Therefore, ΔH_{vap} provides an appropriate estimate of ΔH^{d} .

In addition, Table VII reports ΔH^{ab} of the adsorbates calculated from various methods, including Arnett's expression [Eq. (3)]. For this work, the

Table V Net Retention Times of the Basic IGC Probes for the Treated Glass Bead

T (°C) ($1/K \times 10^3$)	t_N (min)	
	Basic Probes	
	Dimethyl Ketone	Diethylether
85 (2.79)	—	2.84 ± 0.28
90 (2.75)	3.2 ± 0.05	2.44 ± 0.18
100 (2.68)	2.03 ± 0.02	2.00 ± 0.15
110 (2.61)	1.29 ± 0.03	0.79 ± 0.02
120 (2.54)	0.90 ± 0.02	0.65 ± 0.05

emphasis will be on the ΔH^{ab} calculated by using $\Delta H_{\text{vap}}^{\text{CRC}}$ to approximate ΔH^{d} .^{5,15,33}

For the treated glass, the increase in the retention times of the acidic probes (Fig. 3) follows the order of the acidity of the adsorbates ($\text{CCl}_4 < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3$). In contrast, the untreated filler shifts the CHCl_3 curve toward that of the less acidic CH_2Cl_2 (Fig. 6), though the net retention times of both chloromethanes are higher than carbon tetrachloride.

From Table VI, the ΔH_A of the neutral CCl_4 probe for both fillers is higher than the ΔH_{vap} by 2.2 to 3.9 kJ/mol, supporting the *n*-alkane results. Meanwhile, the ΔH_A of CH_2Cl_2 and CHCl_3 for the two glass types range from 10.1 kJ/mol to 17.7 kJ/mol above their respective ΔH_{vap} . This difference is significant and suggests that *both fillers contain basic sites*. However, the treated filler (whose amino groups may be expected to enhance interaction with the CHCl_3) does not exhibit a higher ΔH_A value than the untreated glass.

Examination of the data in Table VII ($\Delta H^{\text{d}} = \Delta H_{\text{vap}}^{\text{CRC}}$) shows that the ΔH^{ab} of the chloro-

Table VI Heats of Adsorption (ΔH_A) of the IGC Probes

Probe	Heats of Vaporization ^a (kJ/mol)	Heats of Adsorption ^b (kJ/mol)	
		Untreated	Treated
CHCl ₃	31.4	42.7 ± 2.9	41.5 ± 2.5
CH ₂ Cl ₂	31.7	49.4 ± 2.1	43.5 ± 2.1
CCl ₄	34.6	38.5 ± 1.3	36.8 ± 1.3
<i>n</i> -Heptane	37.4	42.7 ± 2.5	41.4 ± 1.7
<i>n</i> -Octane	38.6	45.6 ± 3.8	45.2 ± 3.3
<i>n</i> -Propane	20.1	17.7 ^c	17.7 ^c
<i>n</i> -Pentane	27.6	29.5 ^c	29.5 ^c
Acetone	32.0	63.8 ± 3.0	50.5 ± 2.3
Diethyl ether	29.1	63.1 ± 2.8	53.7 ± 2.9

^a Data obtained from Ref. 54.^b Calculated using data from Tables II through Table V and eq. (1).^c Computed using ΔH_A of 5.9 kJ/mol per methylene or methyl group, a value extrapolated from the ΔH_A of *n*-heptane and *n*-octane.

methanes for the untreated glass are within experimental error. However, the trends in the net retention times (Fig. 3) correctly discriminate between CHCl₃ and CH₂Cl₂. As with the *n*-alkanes, the net

retention times prove to be more sensitive in differentiating between two probes whose heats of adsorption are very close, particularly for the treated glass. Furthermore, the higher ΔH^{ab} value of the

Table VII Calculated Enthalpies of Dispersion Interaction (ΔH^d) and Enthalpies of Acid-Base Interactions (ΔH^{ab})

Probe	$\Delta H_{\text{vap}}^{\text{CRC a}}$	$\Delta H_A^{\text{Trouton b}}$	$\Delta H_A^{\text{Riedel c}}$					
A. Enthalpies of dispersion interactions (ΔH^d in kJ/mol)								
CHCl ₃	31.4	30.8	29.7					
CH ₂ Cl ₂	31.7	28.8	—					
CCl ₄	34.6	32.2	29.5					
<i>n</i> -Heptane	37.4	34.2	31.9					
<i>n</i> -Octane	38.6	36.7	34.7					
<i>n</i> -Propane	20.1	21.2	18.8					
<i>n</i> -Pentane	27.6	28.4	25.9					
Acetone	32.0	30.3	30.1					
Diethylether	29.1	28.3	26.4					
	$\Delta H^d = \Delta H_A^{\text{CRC}}$	$\Delta H^d = \Delta H_A^{\text{Trouton}}$	$\Delta H^d = \Delta H_A^{\text{Riedel}}$					
Probe	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
B. Enthalpies of acid-base interactions (ΔH^{ab} in kJ/mol)								
CHCl ₃	11.3	10.1	11.9	10.7	13.0	11.8	7.5	8.0
CH ₂ Cl ₂	17.6	11.7	20.6	14.7	—	—	13.8	9.6
Dimethylketone	31.8	18.5	33.5	20.2	33.7	20.4	34.2 ^e	20.9 ^e
Diethylether	34.0	24.6	34.8	25.4	36.7	27.3	32.1 ^e	22.7 ^e

^a Obtained from Ref. 54.^b Calculated from Trouton's rule.³⁶^c Computed from Riedel's empirical expression using physical constants obtained from Ref. 37.^d Calculated from Arnett's expression [eq. (3)] using CCl₄, *n*-propane, and *n*-pentane as reference probes for the chloromethanes, dimethylketone, and diethylether, respectively.^e ΔH_{vap} for *n*-propane and *n*-pentane taken from Table VI.

CH₂Cl₂ with the untreated glass combination may reflect the interaction of a slightly basic CH₂Cl₂ (owing to the orientation of the chlorine and hydrogen atoms with respect to the carbon atom) with the acidic untreated glass surface.

Correspondingly, the adsorption of both filler types with the basic probes (Figs. 4 and 7) illustrates the complementary characteristic trend, the untreated glass exhibiting stronger interaction with the basic adsorbates. It follows that the net retention times of the untreated filler are higher than those of the treated glass by 8.0 and 86 min at 120°C for diethylether and acetone, respectively. In comparison to the treated glass, the untreated glass strongly attracts the basic probes, reaffirming the preceding results.

For the basic probes, each adsorbate has a ΔH_A at least 18 kJ/mol greater than ΔH_{vap} (Table VI), indicating that *both fillers possess acidic sites as well*. The presence of acidic sites on the *treated* glass surface is not surprising and is consistent with the fact that surfaces tend to be heterogeneous rather than homogeneous, containing both donor and acceptor sites.⁵⁵

Accordingly, the untreated glass is 9.4 and 13.4 kJ/mol more acidic than the treated glass for acetone and diethylether, respectively. *A difference of this magnitude is sufficient to promote or inhibit adsorption of a polymer onto the glass surface*. In this case, the stronger adsorbing basic probes produce greater differences in ΔH_A between the two glass types, providing definitive evidence of the donor-acceptor nature of the glass surface.

Calculation of ΔH^{ab} and Implications of Acid-Base Concepts

From Table VII, the differences in the magnitude of ΔH^{ab} reflects for the most part the differences in the estimation of the dispersion term. As might be predicted by the Drago constants from Table I, the diethylether exhibits slightly higher ΔH^{ab} than ace-

tone. The anomaly in the ΔH^{ab} of the basic probes from Eq. (3) originates from the approximation of ΔH^{d} (ΔH_{vap}) for the *n*-propane reference probe, whose ΔH_{vap} was obtained by extrapolation.

Of more significance is the comparison of the enthalpies of acid-base interactions with those predicted by the Drago equation.⁵⁶ Assuming that the coupling agent, a primary amine, may be represented by methylamine,²⁰ the predicted ΔH^{ab} value for CH₂Cl₂ and methylamine yields 9.3 kJ/mol. This correlates well with the experimental values, ranging from 9.6 kJ/mol [calculated using Eq. (3)] to 11.7 kJ/mol ($\Delta H_{\text{vap}}^{\text{CRC}} = \Delta H^{\text{d}}$). Equation (3) produces the closest value; an expression which has been used by Arnett et al. to determine the heats of formation of hydrogen-bonded complexes.³⁹ Similarly, Koning and Ward, and Koning et al. were able to obtain ΔH^{ab} from Eq. (3) for poly(ethylhexylmethacrylate).^{2,3}

In contrast, for the CHCl₃ probe, the experimental ΔH^{ab} of 11.3 kJ/mol is lower than the predicted value of 21.7 kJ/mol. However, Figure 3 clearly shows the higher net retention times of CHCl₃ relative to the CH₂Cl₂.

For the basic probes, analysis of their retention behavior in Figures 4 and 7 shows that acetone exhibits higher net retention times than diethylether for the same glass type, implying that acetone is more basic than diethylether. Meanwhile, the calculated values of ΔH^{ab} for the diethylether in Table VII are higher than acetone for both glass types (except when ΔH^{d} was estimated using Arnett's equation). The discrepancy may be related to the following factors. First, as evidenced by the heats of vaporization, the dispersion term of acetone is greater than diethylether. A second point concerns the configurational differences between the two molecules. The oxygen atom of acetone is readily accessible for interaction while the oxygen atom of diethylether is more susceptible to shielding by the neighboring hydrogen atoms. The shielding effect

Table VIII Estimated C_A and E_A for the Acidic Sites on the Glass Bead Surface^a

Method of ΔH^{ab} Calculation	Untreated		Treated	
	C_A	E_A	C_A	E_A
$\Delta H^{\text{d}} = \Delta H_{\text{vap}}^{\text{CRC}}$	0.71	6.0	1.6	0.62
$\Delta H^{\text{d}} = \Delta H_A^{\text{TROUTON}}$	0.51	6.9	1.4	1.6
$\Delta H^{\text{d}} = \Delta H_A^{\text{RIEDEL}}$	0.6-0.9	6.0-7.0	1.8	0.72

^a The C_A and E_A parameters for the glass beads were calculated by inserting the C_B and E_B values and heats of acid-base interaction (ΔH^{ab}) of the basic probe (acetone and diethylether) in the Drago equation.

Table IX Comparison of the Estimated E_A and C_A Drago Parameters of the Glass Fillers with Selected Acidic Materials

Material	C_A	E_A
Treated glass ^a	1.6	0.62
Tertiary butanol ^b	0.30	2.04
CHCl_3 ^b	0.150	3.31
Hi-Sil 233 silica ^c	1.16	4.27
Untreated glass ^a	0.70	6.0

^a The Drago parameters were calculated from the ΔH^{ab} of diethylether and dimethylketone ($\Delta H^{\text{d}} = \Delta H_{\text{vap}}^{\text{RC}}$) from Table VII.

^b Obtained from Ref. 20.

^c Obtained from Ref. 51.

would tend to decrease the electron donor capacity of diethylether relative to acetone. It would seem that both factors may play a role.

More importantly, an estimate of the C_A and E_A values of the unmodified and treated glass is possible by utilizing the ΔH^{ab} of the basic adsorbates, the magnitude of ΔH^{ab} being much greater than for the acidic probes. Tables VIII and IX illustrate the C_A and E_A constants calculated from Drago's equation. The variation of the C and E parameter for each type reflects the estimation of the ΔH^{d} term. On the basis of the C/E ratio, the "neat" glass is strongly acidic while the treated glass possesses some weakly acidic sites as well.

For the untreated glass (Table IX), the fact that the Drago constants show it to be more acidic than CHCl_3 is significant because Figure 6 predicts the unmodified glass to be a stronger electron acceptor than CHCl_3 . Evidently, the unmodified glass is more acidic than a silica surface containing hydroxyl groups.⁵¹ The C_A and E_A values will be refined as more data are obtained from a wider range of donor adsorbates. As far as we know, these are the first reported C and E values for fillers determined by the IGC method.

CONCLUSIONS

The IGC results established that the use of low concentrations of probe in the vapor form can characterize the glass filler surface. The unmodified and treated glass bead fillers were found to contain predominantly acidic and basic sites, respectively. More importantly, the results of the neutral probe reaffirm the utility of IGC as a quantitative technique. As expected, the heats of adsorption of the neutral probes were predominantly dispersion-type inter-

actions and were slightly greater than their heats of vaporization. For adsorbates capable of specific interactions, the higher heats of adsorption relative to their respective heats of vaporization were attributed to acid-base interactions between the probe and glass filler surface. Therefore, the retention behavior strongly supports the existence of acid-base interactions between two components that can undergo electron donor-acceptor interactions (untreated glass/oxygen-containing adsorbates and treated glass/chlorocarbons). Furthermore, the heats of adsorption of the basic probes (dimethyl ketone and diethylether) with the two glass types differed by at least 9.4 kJ/mol. A difference of this magnitude is sufficient to promote or inhibit adsorption. Therefore, the IGC results indicate two glass bead filler surfaces whose acid-base characteristics are different from one another.

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REFERENCES

1. F. Chen, *Macromolecules*, **21**, 1640 (1988).
2. P. A. Koning and T. C. Ward, Presented at the ACS Annual Meeting, Anaheim, CA, Sept. 1986.
3. P. Koning, T. C. Ward, R. D. Allen, and J. E. McGrath, *Polymer Preprints*, **26**(1), 189 (1985).
4. C. Richard, K. Hing, and H. P. Schreiber, *Polym. Comp.*, **6**(4), 201 (1985).
5. A. C. Tiburcio and J. A. Manson, Office of Naval Research, Contract No. N00014-79-C-0731, Annual Report, Lehigh University, Bethlehem, PA, January 1986.
6. January 1984.
7. C. Saint Flour and E. Papirer, *J. Coll. Int. Sci.*, **91**(1), 69 (1983).
8. C. Saint Flour and E. Papirer, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**(4), 666 (1982).
9. H. P. Schreiber, M. R. Wertheimer, and M. Lambla, *J. Appl. Polym. Sci.*, **27**, 2269 (1982).
10. H. P. Schreiber, *Org. Coat. Appl. Polym. Sci.*, **45**, 22 (1982).
11. C. S. Chamberlain and R. S. Drago, *J. Am. Chem. Soc.*, **101**, 5240 (1979).
12. J. E. G. Lipson and J. E. Guillet, *Developments In Polymer Characterization*, J. V. Dawkins (Ed.), Applied Science, New Jersey, 1982, Vol. 3, Chap. 2.
13. J. R. Conder, and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, New York, 1979.
14. S. A. Greene and H. Pust, *J. Phys. Chem.*, **62**, 55 (1958).

15. J. Anhang and D. G. Gray, *J. Appl. Polym. Sci.*, **27**, 71 (1982).
16. G. Di Paola-Baranyi and J. E. Guillet, *Makromol. Chem.*, **181**, 215 (1980).
17. A. B. Littlewood, C. S. G. Phillips, and D. T. Price, *J. Chem. Soc.*, 1480 (1955).
18. F. M. Fowkes and M. A. Mostafa, *Ind. Eng. Chem. Prod. Res. Dev.*, **17**, 3 (1978).
19. R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).
20. R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **93**(23), 6014 (1971).
21. J. R. Conder, D. C. Locke, and J. H. Purnell, *J. Phys. Chem.*, **73**, 700 (1969).
22. H. L. Liao and D. E. Martire, *Anal. Chem.*, **44**(3), 498 (1972).
23. D. F. Cadogen and J. H. Purnell, *J. Am. Soc. A*, **9**, 2133 (1968).
24. D. E. Martire, *Progress in Gas Chromatography*, J. H. Purnell (Ed.), Interscience, New York, 1968, pp. 93–120.
25. D. E. Martire and P. Riedel, *J. Phys. Chem.*, **72**(10), 3478 (1968).
26. J. R. Conder, *J. Chromatogr.*, **39**, 273 (1969).
27. D. F. Cadogen and J. H. Purnell, *J. Phys. Chem.*, **73**, 3849 (1969).
28. C. S. Chamberlain and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 6142 (1976).
29. H. L. Liao and D. E. Martire, *J. Am. Chem. Soc.*, **96**(7), 2058 (1974).
30. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
31. H. P. Schreiber, Y. B. Tewari, and D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 15 (1973).
32. C. S. Su, D. Patterson, and H. P. Schreiber, *J. Appl. Polym. Sci.*, **20**, 1025 (1976).
33. Darryl Williams, Imperial College, London, England, 1986, private communication.
34. G. M. Dorris and D. G. Gray, *J. Phys. Chem.*, **85**, 3628 (1981).
35. G. M. Dorris and D. G. Gray, *J. Coll. Int. Sci.*, **77**, 353 (1980).
36. W. J. Moore, *Physical Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1972, p. 213.
37. L. Riedel, *Chem. Ing. Tech.*, **26**, 679 (1954).
38. J. M. Smith and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 3rd ed., McGraw-Hill, New York, 1975, p. 115.
39. E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. V. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2365 (1970).
40. V. Gutman, *Coord. Chem. Rev.*, **2**, 239 (1967).
41. V. Gutman, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press, New York, 1978, p. 19.
42. J. M. Braun and J. E. Guillet, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1073 (1976).
43. O. Smidsrod and J. E. Guillet, *Macromolecules*, **2**(3), 272 (1969).
44. M. A. Llorente, C. Menduina, and A. Horta, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 189 (1979).
45. D. D. Desphande and O. S. Tyagi, *Macromolecules*, **11**, 746 (1978).
46. M. Galin and J. E. Guillet, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 233 (1973).
47. J.-M. Braun and J. E. Guillet, *Macromolecules*, **9**, 340 (1976).
48. J. Klein and H. Widdecke, *J. Chromatogr.*, **147**, 384 (1978).
49. J.-M. Braun and J. E. Guillet, *Macromolecules*, **10**, 101 (1977).
50. A. C. Tiburcio and J. A. Manson, Office of Naval Research, Contract No. N000-14-79-C-0731, Annual Report, Lehigh University, Bethlehem, PA, Dec. 1984.
51. D. C. McCarthy, Ph.D. Dissertation, Lehigh University, Bethlehem, PA, 1984.
52. J. J. Pesek and J. A. Graham, *Anal. Chem.*, **49**, 133 (1977).
53. S. Joslin, Ph.D. Dissertation, Lehigh University, Bethlehem, PA, 1984.
54. *CRC Handbook of Chemistry and Physics*, Robert C. Weast (Ed.), CRC Press, Boca Raton, FL, 1979.
55. C. Vidal-Madjar and G. Guichon, *J. Phys. Chem.*, **71**, 4031 (1967).
56. R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**(16), 3572 (1965).

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