Probe Selection and Description in IGC: A Nontrivial Factor

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ABSTRACT: Inverse gas chromatography (IGC) has found many uses in the characterization of polymer surfaces and their interaction capabilities. The IGC method relies on the selection of vapors with which to probe polymer surfaces. Problems attached to the volatile phase in IGC are considered. One of these is the temperature dependence of the probe molecule dimensions. Experimental work shows that correcting for this temperature dependence is recommended when IGC work is carried out at temperatures removed from the ambient by more than 30°C. A second problem area is a possible variation in the orientation of adsorbed probe molecules. The variable orientation of linear alkane probe molecules on a polystyrene substrate is demonstrated, as is an orientational degree of freedom when diols of varying chain lengths are adsorbed on polymeric as well as on inorganic substrates. A conclusion reached from the experiments of this work is that acid–base parameters generated by the IGC method have relative but not necessarily absolute significance. Further, the orientation of polar probe molecules is dependent on the force field generated by the underlying substrate, which may be characterized by its total surface free energy. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2323–2330, 2003

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INTRODUCTION

Inverse gas chromatography (IGC), sometimes (and arguably more accurately) called molecular probe chromatography (MPC), has seen a rapid rise in its varied applications to polymer systems. The experimental technique is disarmingly simple, differing from conventional gas chromatography only in the placement of an "unknown" solid in the stationary phase. When that solid is probed by a highly dilute stream of vapor molecules entrained in a noninteracting carrier gas, the interaction between solid and vapor results in a partitioning of the vapor species and the resultant measurement of a retention time. With appropriate corrections, frequently reported in detail,[1–3] a specific retention volume, Vn, may then be calculated. This opens the route to an evaluation of a wide variety of parameters descriptive of the stationary phase. Much use has been made of this for the characterization of polymer properties. Examples include the measurement of glass transition temperatures,[3] meaningful determinations of the solubility parameter for polymers,[4] and similarly realistic determinations of the Flory–Huggins interaction parameter for solid/vapor pairs, $\chi_{1,2}$. An extension to the measurement of thermodynamic interaction parameters for mixed stationary phases $\chi_{2,3}$,[5] while not without inherent difficulties,[6] nevertheless can be very useful in defining miscibility/immiscibility boundaries in polymer blends.[7] By choosing both polar and nonpolar probe vapors, it is possible to separate dispersion, or Lifschitz–van der Waals (L/W) interactions between the polymer and vapor, from interactions involving nondispersion forces. Following the procedures exemplified by Fowkes[8] and Good and coworkers,[9] among others, nondispersion interactions are termed "acid–base" interactions. The subject of acid–base interactions in polymer systems has seen very rapid growth; a recent review[10] highlighted some of the progress made in the field. The present article, in part review and in part the source of new information, draws attention to the choice of a descriptor used to characterize the vapor phase. The matter of choice is a nontrivial aspect of IGC methodology; in one respect, it places limitations on the absolute value of the information drawn from the experiment. In another, however, it enriches the data base attainable from the protocol.

Vapor-phase descriptor, L/W, and polar interactions

The thermodynamic significance of Vn is evident from the relation between the chromatographic datum and

the free energy of desorption of the vapor probe, ΔGa. When the vapor phase is extremely dilute, then adsorption follows Henry's law:

$$\Delta Ga = -RT \ln [c\, Vn/A\, m] \qquad (1)$$

where R is the gas constant; T, the absolute temperature; A, the specific surface area of the solid (stationary phase); m, its mass; and c, a constant dependent on the choice of reference state. When only L/W forces can act between vapor and solid, for example, when n-alkanes are the probe molecules, then the experimental data lead directly to an evaluation of the dispersion component of the solid's surface energy, γ_s^d. Two statements have been made for the purpose: According to Dorris and Gray,[1]

$$\gamma_s^d = (\Delta G_{CH2})^2/4N^2 a_{CH2}{}^2 \gamma_{CH2} \qquad (2)$$

Here, N is Avogadro's number, $a_{CH2}(= 0.06 \text{ nm}^2)$ is the area of an adsorbed CH_2 unit, γ_{CH2} is the surface energy of the methylene group (generally equated to that of linear polyethylene, at 35.5 mJ/m^2 under ambient conditions), and ΔG is obtained experimentally from a straight-line plot of the free-energy datum for a number of alkanes versus the number of their carbon atoms. An alternate route[11] is given by

$$RT \ln Vn = 2N a\, (\gamma_s^d)^{1/2}\, (\gamma_l^d)^{1/2} + C \qquad (3)$$

In this statement, a represents the area occupied by the adsorbed molecule, γ_l^d is the surface energy of the vapor in the corresponding liquid state (clearly, in the case of alkanes, this will equal the total surface energy of the compound), and C is a constant, again dependent on the selection of the reference state. A plot of $RT \ln Vn$ versus the product $a\, (\gamma_l^d)^{1/2}$, for a series of n-alkanes, should generate a straight line, from the slope of which may be obtained the γ_s^d value. The straight line also represents a reference from which to obtain ΔG^{ab}, the acid–base (polar) contribution to the free energy of desorption, relevant to an experiment using polar vapors as probe species. These vapors generally are chosen on the basis of their acid–base characteristics, as defined by contemporary theories. In much of the published work, the theory of choice has been that of Gutmann,[12] in which acceptor (AN) and donor (DN) numbers are assigned to a set of organic vapors suitable for IGC application. By extending the IGC work over a suitable temperature range, it is possible to evaluate the enthalpy of acid–base interactions between vapor and solid, ΔH^{ab}, and, finally, by combining the enthalpy and AN and DN numbers, we may obtain acid–base interaction parameters, Ka and Kb, for the stationary phase. Following published literature,[11,13] we write

$$\Delta G^{ab} = RT \ln (Vn)/(Vn)_{\text{ref}} \qquad (4)$$

where the reference is the retention volume of an L/W (e.g., alkane) probe with the same a value as that of the polar probe in question. As usual, we can then state that

$$\Delta G^{ab}/T = \Delta H^{ab}/T - \Delta S^{ab} \qquad (5)$$

yielding the needed enthalpy datum, and, finally,

$$\Delta H^{ab} = Ka\, DN + Kb\, AN \qquad (6)$$

The Ka and Kb parameters have been used with considerable success to rationalize polymer properties, ranging from the effects of surface treatments on the interaction behavior of reinforcing fibers[14] to the dispersion and stability of pigments in polymer-coating formulations[15,16] and to a relationship with the interfacial tension between pairs of polymers.[17] Yet, the success must be moderated with caution, since an absolute value for a is somewhat equivocal. One of the problems is associated with the wide range of temperatures over which IGC experiments can be conducted. Tabulated values of cross-sectional areas of probes generally used in IGC are given for near-ambient temperatures, so that a method of accounting for the dependence of molecular dimensions on temperature is advisable. Practical approaches to the challenge have been suggested.[18,19] In this instance, we follow that stated by Donnet and coworkers.[18] Involved is the known density–temperature variation for alkanes and other organic molecules used in IGC. Using the appropriate density value, the temperature variation of a can then be estimated from

$$a = [2L/\sqrt{3}]^{1/2} [M/\rho\, N]^{1/2} \qquad (7)$$

where L, M, ρ, and N are the molecular length, mass, and density and the Avogadro number, respectively. The magnitude of errors involved by ignoring $\partial a/\partial T$ was studied by Mukhopadhyay and Schreiber.[20] An updated version of their earlier work is given in Table I; the polymer is a styrene-co-maleic anhydride (PSMA), with 26 wt % MA content. Although the error committed by ignoring the temperature effect is unimportant within about 30°C of ambient, it becomes significant at temperatures higher than 60°C and clearly should be taken into account when working at temperatures well removed from the ambient.

A more serious problem associated with the use of the a parameter is that of molecular orientation, a matter which is discussed more fully later in this article. The use of nonspherical probe molecules clearly raises the question of the molecule's configuration when in close contact with the substrate. In

TABLE I
Effect of Temperature Correction to a Value on γ_s^d

Measurement	T (°C)							
	30	40	50	60	80	90	100	110
$(\gamma_s^d)^a$	39.3	33.8	33.3	27.9	23.1	19.8	18.7	14.5
$(\gamma_s^d)^b$	40.3	34.6	34.1	28.8	25.7	22.0	20.7	16.2
% Error	2.5	2.4	3.6	3.2	11.3	11.1	10.7	11.2

Polymer is PS-*co*-MA.
γ_s^d was computed from IGC data using *n*-alkane vapor probes.
Data after ref. 20.
[a] Based on a values at 25°C.
[b] Based on a values corrected for T variation of alkane densities.

part, the issue depends on the force field exerted on the probe molecule by the solid. As pointed out in recent publications,[10,21–23] almost all solid surfaces are heterogeneous and possess finite site-energy distributions. Thus, it may be expected that the probe molecules may adopt a range of configurations depending on the energies of sites with which they interact. Indeed, a combination of extreme-dilution and finite-concentration IGC (in the latter variation, finite amounts of probes are injected) can be used to estimate the degree of surface heterogeneity in sites interacting by L/W forces as well as in those interacting by polar (acid–base) forces.[24] The central issue, however, is the implied variation in a values corresponding to the range of configurations attainable by the adsorbed molecule.

One way of sidestepping the matter is to select other molecular descriptors for the volatile phase. Among the alternatives to a which have been used are the saturation vapor pressure of the probe, p_1^0, under relevant T conditions,[11,25] and the normal boiling temperature, T_b.[26] The formal link between the retention data and the thermodynamic interaction parameters is affected by these choices, but an empirical comparison of data is nevertheless instructive. Working with polycarbonate (PC) as the substrate, the three alternatives to probe characterization were used[27] to obtain apparent values of the dispersion surface energy, of ΔH^{ab}, and of the acid–base interaction parameters Ka and Kb for the polymer. The earlier data for polar interaction were reconfirmed using new polymer samples, and the results of the newer investigation are given in Table II. Clearly, the choice of the descriptor is (in this instance) noncritical. The interaction enthalpy for each of the polar probes is essentially constant within experimental uncertainty and thus may be considered as independent of the descriptor used. Similarly, the Ka and Kb parameters display only minor variations and again appear to be insensitive to the selection of the probe descriptor. Thus, to avoid potential difficulties with ill-defined adsorption areas, the vapor pressure or boiling temperature descriptors may find some favor. Of course, a wider range of substrates should be

used in similar comparisons in order to place the question of probe descriptor on a firmer footing.

EXPERIMENTAL

In this section, we report the results of our current work. This is directed, in part, to the manner in which the Ka and Kb parameters for polystyrene (PS), poly-(vinyl chloride) (PVC), PC, and an organic pigment respond to the selection of acid and base vapor probes and, in part, to the effects of apparent configurational variations in alkane and polar probes on γ_s^d and on ΔG^{ab} with PS as the stationary phase.

Acid–base characterization and the selection of vapor probes

The usual route to the determination of Ka and Kb parameters by IGC is to use a series of, typically, five or more vapors representing the acid, base, and amphipatic category, as defined by the Gutmann theory.[12] The various ΔG^{ab} values obtained over a narrow range of temperature then lead to a ΔH^{ab} value. The plot of $\Delta G^{ab}/T$ versus $1/T$, dictated by eq. (5), is fitted with a straight line, generating an averaged enthalpy value. This, however, may mask any significant variation in the acid–base interaction parameters that may

TABLE II
Interaction Parameters from IGC Using Diverse Probe Descriptors

Probe descriptor Vapor probe	$-\Delta H^{ab}$ (kJ/mol)		
	a	p^0	T_b
Diethyl ether	48.1	50.0	49.2
Acetone	51.7	47.0	50.6
Chloroform	39.2	40.0	40.4
Tetrahydrofuran	46.7	48.4	46.4
Ethyl acetate	52.5	52.1	51.0
Ka	0.88	1.02	0.96
Kb	3.3	3.3	3.5
Ka/Kb	3.8	3.2	3.6

Polymer is PC; IGC data from 100–120 °C.
Table After ref. 27.

result from specific choices of polar vapor probes. The concept was studied in this sequence using four stationary phases and pairs of acid and base probes with widely differing (Gutmann) AN and DN indexes. The probes and their interaction indexes are identified below. The values are from Gutmann's tabulation[12]; DN is expressed in kcal/mol:

Probe	AN	DN
Chloroform (symbol CHL)	23.1	0
Benzene (BZ)	8.2	0.1
Diethyl ether (DEE)	3.9	19.2
Tetrahydrofuran (THF)	8.0	20.0

Three polymers and an organic red pigment served as stationary phases. The polymers were PS, PVC, and PC. PS was obtained from the Amoco Corp (Napperville, IL). An M_w value of 87,000 and an M_w/M_n ratio of 1.2 were reported, as evaluated by gel-permeation chromatography. The PVC resin, obtained from Synergistics Canada Ltd. (Napierville, QC), had a viscosity-average molecular weight of 66,000. It contained no additives. PC (Lexan 140), supplied by General Electric Co. (Schenectady, NY), was the same polymer as used in earlier work.[27] The pigment, PR, also used in previous work,[24] was an uncoated diketo pyrrolo pyrol red with a surface area of 29 m^2/g, as determined from nitrogen adsorption (BET) measurements. The pigment density was 1.6 g/mL.

The polymers were coated onto a Chromosorb AW 60/80 mesh support from solutions. The solvents used were toluene for PS and methyl ethyl ketone for both PVC and PC. The solutions contained approximately 2 wt % of polymer solutes. Following evaporation to dryness, coated solids underwent conventional drying and ashing procedures to determine the mass of the retained polymer. These showed that 9.4 wt % PS, 8.0 wt % PVC, and 8.8 wt % PC were supported by the Chromosorb, sufficient in each case to ensure full, multilayer surface coverage of the support. Coated solids were packed in degreased, washed, and dried stainless-steel columns, 1.2 mm in diameter and 40–60 cm long. The pigment was packed directly into a similarly conditioned stainless-steel column, 2.4 mm in diameter and 30 cm long. The mass of pigment utilized was 0.716 g. A Varian 3400 chromatograph, equipped with hot-wire and ionizing flame detectors, was used throughout the study. Columns were equilibrated at 55, 60, and 65°C and at each temperature were swept with He carrier gas for about 4 h prior to commencing retention measurements. Following the establishment of reference lines with n-alkanes (nC6—nC9) as the probes, pairs of polar probes were injected at "infinite" dilution to effect measurement of the Ka and Kb parameters. These are taken to represent the properties of the stationary phases at the mean temperature of 60°C. Retention volumes for each probe

were obtained in at least triplicate, with experimental uncertainties not exceeding 3%. The Ka and Kb data, given in Table III, are considered to be accurate within 10% of the stated values. In the experimental procedure, following the collection of data for each probe pair, the column T was increased to 75°C and the stationary phases were swept with He carrier gas for a minimum of 3 h. Periodic injections of nC6 as a reference probe were used to ensure that the retention volume of this marker remained within at least 3% of the datum obtained before any of the polar probes were injected. Thus, each acid–base probe pair may be considered to scan the stationary-phase surfaces in identical states.

The results in Table III indicate clearly that each pair of acid (A) and base (B) probes generates somewhat different sets of Ka and Kb values. In the case of PS, the combination of CHL and THF produces a significantly stronger interaction, both Ka and Kb exceeding the corresponding values generated by the BZ/THF and BZ/DEE combinations. The degree of variation in PVC and PC is somewhat less, but still greater than would be expected on the basis of experimental uncertainty alone. In the organo-red, PR pigment, the variation is similar to that found for PS. Of prime interest, however, is the constancy in each of the cases of the Ka/Kb ratio. It appears then that individual Ka and Kb values should be accorded relative, but not absolute significance, since the measured values will depend on the exact selection of interacting probes. However, any given combination of A and B probes will place substrates into the same relative position on an acidity–basicity scale.

Interaction parameters and orientation of molecular probes

In an earlier section of this article, the problem of the orientation of adsorbed probe molecules was raised in connection with the relevant value of a to be used in

TABLE III
Acid–Base Parameters: Sensitivity to Probe Selection

Solid	A probe	B probe	Ka	Kb	Ka/Kb
PS	CHL	THF	1.1	3.7	0.30
PS	BZ	THF	0.7	2.3	0.30
PS	BZ	DEE	0.8	2.6	0.31
PVC	CHL	THF	4.4	2.5	1.76
PVC	BZ	THF	4.0	2.2	1.82
PVC	BZ	DEE	3.7	2.0	1.85
PVC	CHL	DEE	4.1	2.3	1.78
PC	CHL	THF	2.7	3.8	0.71
PC	CHL	DEE	2.2	3.4	0.65
PC	BZ	DEE	2.6	3.7	0.70
PR	CHL	THF	0.9	0.5	1.80
PR	BZ	DEE	1.3	0.7	1.85
PR	BZ	THF	1.4	0.8	1.75

computations of surface energies and interaction parameters for a (polymer) stationary phase. An obvious manifestation of the difficulty might be expected when a series of alkane probes is used to evaluate γ_s^d. For short-chain members of the alkane series, the orientational state of the probe may not be important, since much the same area of the surface will be covered whether the probe is in a head-to-tail configuration normal to the surface or lying at some angle to the substrate. In longer-chain homologs, however, the area screened by the probe molecule will begin to vary significantly with its orientational angle. Given that polymer surfaces, like solid surfaces in general, are heterogeneous,[21,28] it follows that adsorption will initially occur preferentially on the most energetic surface sites. If these are distributed randomly over the surface, then larger chain molecules, even if primarily associated with the high-energy sites, will, nevertheless, interact with a broader segment of the site energy distribution than will small-chain homologs. As a result, variation in the surface energy value might ensue. This consideration motivated one series of the experiments discussed in the present section. Configurational effects also may contribute to the measurement of parameters associated with the use of polar probes. For example, a significant difference could arise in the ΔG^{ab} datum, depending on how the probe is oriented to the substrate. A second series of experiments was conducted to question this.

Throughout the work in this section, one of the stationary phases was the PS sample already described above. Polypropylene (PP) and a calcium carbonate were also employed, as discussed later in the section. The temperature was maintained constant at 60°C in all cases. In the first experimental sequence, involving PS only, the procedures followed were those which normally lead to the establishment of a reference line descriptive of the L/W interaction between the polymer and *n*-alkane probes [see eq. (3)]. However, instead of using several alkane probes to obtain a generalized linear function according to eq. (3), from which a value of γ_s^d is obtained, in this work, the surface energy datum was determined from a series of trials in which consecutive pairs of alkanes served as probes. Thus, at one extreme of the sequence, the surface energy was calculated from data generated by the pair nC4 and nC5, and at the other extreme, the probes were the long-chain pair nC11–nC12. Probes were injected at extreme dilution throughout the work. Reproducibility of retention volumes, again determined in at least triplicate, was better than 4%. The experimental uncertainty also applies to the γ_s^d values, reported in Table IV. The relevant column in the table also states the surface energy value as measured by static contact-angle data. In these, the volume of contacting droplets was 10 μL.

TABLE IV
Alkane Probe Selection and Effect on γ_s^d Datum for PS and Suggested Orientation of Adsorbed Probe Molecule

Alkane probes	γ_s^d (mJ/m^2)	Orientation to surface (°)
nC4—nC5	38.1	90[a]
nC5—nC6	37.7	68
nC6—nC7	37.4	66
nC7—nC8	37.3	65
nC8—nC9	36.8	45
nC9—nC10	36.4	32
nC10—nC11	36.1	22
nC11—nC12	35.8	12
Contact angle	35.5	0[b]

Data refer to $T = 60$ °C.
[a] Assumed value.
[b] Assigned value.

There is an evident and substantial decrease in the surface energy as the chain length of the probe pairs increases. Finally, the values reported by alkanes greater than about nC10 are within the experimental uncertainty of the value obtained from the contact-angle measurements. Assuming that 10 μL of the droplets contact a broad cross section of available surface sites, the value of 35.5 mJ/m^2 may be taken as the average γ^d for the PS specimen. The vapor probes injected at extreme dilution would, of course, associate with higher-energy sites of the distribution, so that the difference between the contact angle and the alkane probe data may be viewed as an indication of energy heterogeneity in L/W sites of the polymer surface. In this context, the IGC procedure yields results analogous to the surface energy heterogeneity indexes evaluated from comparisons of infinite dilution and finite concentration injections of probe molecules.[29] Since in the present instance probes were injected always at extreme dilution, the decrease of the γ_s^d datum may be attributed to varying orientations of the adsorbed alkane molecule. Clearly, a molecule lying flat on the surface would interact with a broader range of site energies than would the same molecule oriented normal to the surface. To put this concept in perspective, it was assumed that the shortest-chain pair of alkanes (nC4, nC5) would indeed adsorb in a configuration normal to the surface, thereby subtending an orientational angle of 90°. Droplets of alkane liquids, such as used in contact-angle determinations, are known to spread on the PS surface and may, therefore, be assigned an orientational angle of 0°. From these assumptions, it is then possible to estimate, by interpolation, the orientational angle of the various alkane pairs required to account for the observed surface energies. For example, the pair nC8–nC9 reports a γ^d which is midway between the data for the droplets and for the limiting nC4–nC5 combination. Accord-

ingly, it is assigned an orientational angle of 45°. The computed data are given in the final column of Table IV.

In the example given, only inherently weak dispersion forces can act between the surface and the probe. Presumably, these are insufficient to maintain the adsorbed species in closely packed arrays and may therefore be held responsible for the decrease in angle subtended by increasingly long alkane chains. It was felt that the use of polar probes could further inform on questions of orientation and on the consequences to measured surface characterization parameters arising from different orientations of the adsorbed molecules. Accordingly, in a second experimental sequence, at first restricted to the PS substrate, six diols of increasing n-alkane chain length from ethane to octane (but omitting the heptane member) were used as probes. The reagent-grade chemicals were obtained from the Aldrich Chemical Co. (Milwaukee, WI) and used as received. Again, injection was at extreme dilution, with retention volumes measured with a reproducibility of better than 4%. Following use of any one of the diols, the PS surface was swept with He at 75°C and, as already stated earlier, injections of the marker nC6 probe were used to ensure that the polymer surface was in its initial state prior to injecting another in the diol series. In the light of results obtained, the inquiry was broadened to include a nonpolar polymer substrate and the inorganic filler. The PP in use was obtained from the Shell Chemical Co. (Toronto, Canada). An $M_w = 144,000$ and an $M_w/M_n = 3.8$ were reported, as determined by size-exclusion chromatography. The CaCO₃, from Aldrich Chemical Co., was
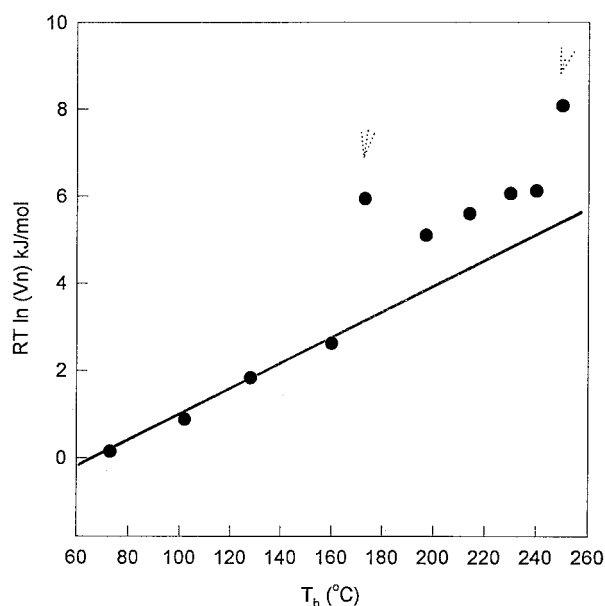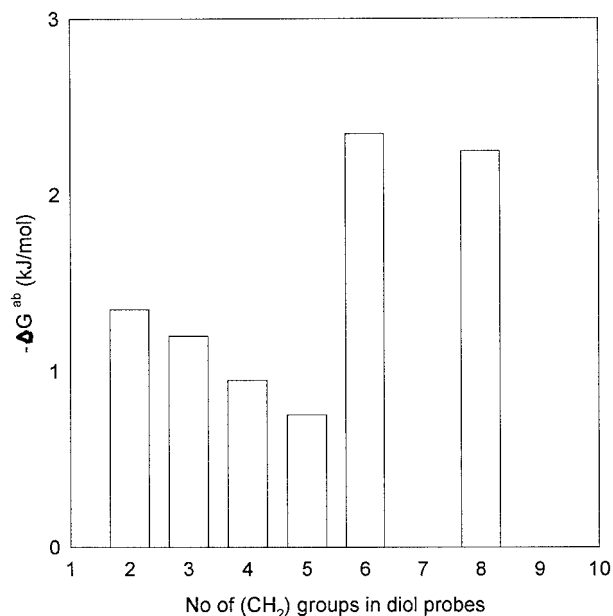

Figure 2 Variation of acid–base free energy of desorption of alkane diol probes with alkane chain length, with PS at 60°C as stationary phase.

uncoated and had a surface area of 2.6 m²/g. The IGC protocols described above were also applied in these cases.

Considering the PS stationary phase first, the position of the diol probes relative to the reference line generated by alkanes is given in Figure 1. The T_b probe descriptor is used here, so as to avoid any confusion arising from a possible variation in a in a traversal of the diol series. Expectedly, the diols fall well off the L/W force reference line, attesting to the capability of PS to interact through electron donor/acceptor exchanges. Of principal concern is the placement of the hexane and octane diols, identified by arrows in Figure 1. When compared with the retention data for diols from ethane through pentane, the distance from the L/W force reference line for the longer-chain diols roughly doubles. The apparent variation of ΔG^{ab} with the diol chain length is shown more clearly in the bar graph of Figure 2. An attractive, albeit tentative, explanation of the results again hinges on the orientation of the adsorbed volatile phase molecules. Chains up to the pentane diol may be considered too short to permit both terminal polar groups to interact with the surface. The chains therefore may be oriented to the PS in a head-to-tail configuration. The slight decrease in ΔG^{ab} with increasing chain length possibly may arise from increasing interactions between the free hydroxyls of the adsorbed diol chains. In terms of this account, in hexane and octane diols, both terminal OH groups are able to contact the surface. An apparent mechanism for this would be to have these molecules lie flat on the PS surface, thereby generating ΔG^{ab}

Figure 1 Plot of $RT \ln Vn$ versus T_b for n-alkane and alkane diol vapor probes on PS at 60°C. Arrows identify positions of hexane and octane diol probes.

values about double those for the shorter-chain homologs.

A test for the broader applicability of the orientation hypothesis was provided by data for PP and CaCO$_3$ as stationary phases. The relevant ΔG^{ab} data are displayed in Figure 3. The polar filler substrate generates specific interaction parameters which, while greater than those seen in Figure 2, parallel the PS data exactly. There is, once again, a slight decrease in ΔG^{ab} for diols in the ethane through the pentane series, and the parameter is roughly doubled when hexane and octane diols are the vapor probes. Apparently, very similar orientation effects are operative. The data for PP are, however, entirely different. Here, the interaction datum is small and presumably due solely to the somewhat greater L/W force associated with contact between the polyolefin and OH groups than for contact with the probe's methylene groups. Little information on the orientation of the probe molecule is to be obtained in this instance. The relatively large difference between ΔG^{ab} values for PS and CaCO$_3$ suggests that the strength of the substrate force field may be implicated in the configuration taken up by the probe molecule. The orienting potential of the substrate may be represented by the surface energy, a datum available for the three substrates of this inquiry. Further, we now suggest, on the basis of data shown in Figures 1– 3, that the short-chain diols assume a head-to-tail configuration on the substrates. If the ΔG^{ab} values in Figures 2 and 3 for diols in the ethane-through-pentane series are extrapolated to the

Figure 4 Influence of stationary phase surface energy on excess value of acid–base free energy of desorption, suggesting that vapor probe orientation is dependent on the force field exerted by the substrate with which it interacts. Solids are CaCO$_3$, PS, and PP.

positions of the hexane and octane diols, they identify a calculated value $(\Delta G^{ab})_{calc}$ which differs from $(\Delta G^{ab})_{exp}$, the experimental counterpart. The difference, ostensibly due to the changed configuration of the hexane and octane diols, is shown as function of the substrate surface energy in Figure 4. The $[(\Delta G^{ab})_{exp} - (\Delta G^{ab})_{calc}]$ for hexane and octane diol are indistinguishable; accordingly, they are represented in the figure by a single point. The suggestion of a relationship mandates a fuller inquiry into the role played by the substrate force field in deciding the configuration of adsorbed molecules. IGC, yet again, appears to offer a viable route to the goal.

CONCLUSIONS

The following may be concluded:

- Vapor probe description is a recognized variable in the IGC protocol. In the case of a styrene maleic anhydride copolymer, however, description of the stationary phase was effectively identical for three different methods of characterizing the vapor probes. This suggests that the probe descriptor effect is of limited significance to the determination of the surface energy and the acid–base interaction parameters for the polymer.
- When using a, the area of cross section of the adsorbed vapor probe, it was shown advisable to correct the descriptor for T-dependence, when IGC measurements were conducted at temperatures more than 20–30° above ambient.
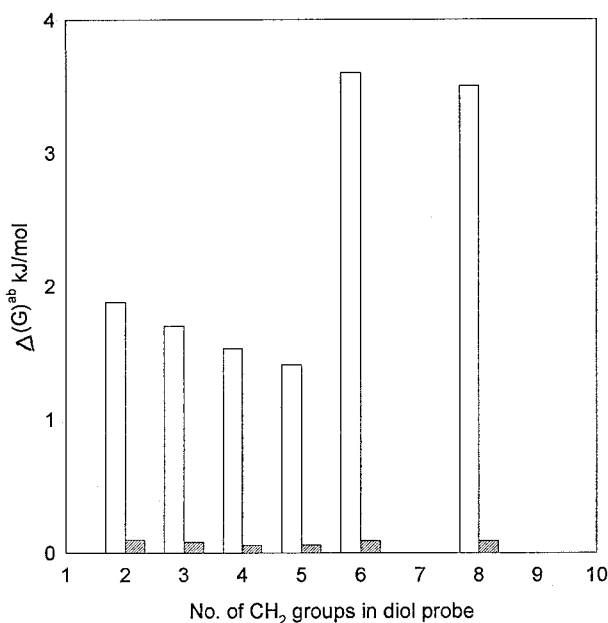

Figure 3 Variation of acid–base free energy of desorption of alkane diol probes with alkane chain length. Stationary phases are (open columns) CaCO$_3$ and (shaded columns) PP, both at 60°C.
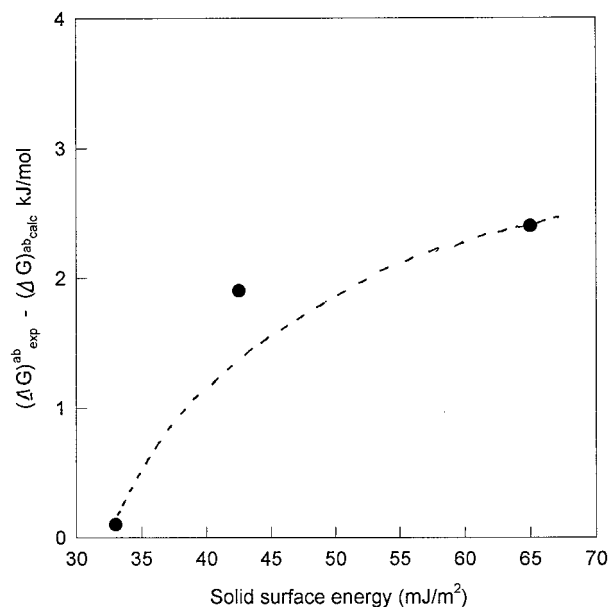
- Acid–base interaction values (*Ka* and *Kb*) for the stationary phase have been shown to vary with the selection of the acid and base vapor probes. *Ka* and *Kb* therefore are accorded relative but not absolute significance. However, any set of probes rates solids in a consistent manner on an acid–base scale.
- Variations in the orientation of both L/W and acid–base probes have been documented. The variations arise due to the site energy heterogeneity of polymer and nonpolymer solids and may be used as a tentative measure of the scale of surface heterogeneity.

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