A Gas Chromatographic Method for the Study of Sorption on Polymers

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ABSTRACT: A simple procedure for determining adsorption isotherms from the shape of single gas chromatographic peaks was applied to poly(methyl methacrylate) and polystyrene surfaces using *n*-decane and *n*-hexanol as sorbates. At high sorbate concentrations, the resultant isotherms were nonlinear, due primarily to surface saturation. Reasonable estimates of the surface area were obtained by a BET treatment of the isotherm shape in this concentration region. At sufficiently low sorbate concentrations on poly(methyl methacrylate), peak retention volumes were independent of the amount of sorbate, so that relative surface areas and sorption enthalpies were readily obtained under appropriate conditions.

Gas chromatographic methods have been shown to provide useful information on the transition temperatures[1,2] and crystallinity[3,4] of polymers and on the thermodynamics of polymer–solute interactions.[5,6] Recently the surface characteristics of polymers have been investigated by this method.[7-10] In this paper some aspects of the interaction of a "probe" molecule with a polymer surface contained in a gas chromatographic column are examined to determine the applicability of gas–solid chromatographic methods[11] to polymeric substrates.

In previous work, the interaction of the probe molecule with the polymer was measured by its specific retention volume,[12] a fundamental gas chromatographic parameter independent of experimental conditions and depending only on the column temperature and the chemical nature of the polymer and probe molecules. In particular, meaningful retention volumes should be independent of the size of the injected probe sample. This was found, for example, with dodecane dissolved in polyethylene[3] and implies that the equilibrium concentrations in the polymer and in the gas phase are linearly related for sufficiently dilute solutions. However, when retention of the probe is due to adsorption on the surface of a solid rather than in solution, the isotherms relating concentrations in the gas phase and on the surface are often curved owing to surface heterogeneity and to incipient saturation of the available sites. Furthermore, the sample sizes normally injected in gas chromatography often span a considerable portion of the isotherm, so it is not always possible to work at concentrations of probe low enough to ensure effective linearity. Retention volumes in this case depend on sample size, so that the shape of the isotherm must also be determined in order to characterize the adsorbate–adsorbent interaction.

Gas chromatographic techniques have been widely used to determine adsorption isotherms.[11,12] While most work has involved the use of a "frontal" technique,[13] it is also possible to use the conventional elution technique and from a single unsymmetrical peak to determine the shape of the isotherm.[14] Starting from the first-order conservation equation of chromatography,[15] it may be shown that for each gas-phase concentration c of eluted probe vapor, there exists a corresponding retention volume V_c given by

$$a = \frac{1}{m}\int_0^c V_c \mathrm{d}c \qquad (1)$$

where a is the amount of probe vapor adsorbed on a mass m of adsorbent. In the absence of all peak-broadening factors other than the nonlinearity of the isotherm, one side of the elution peak should be vertical while V_c may be determined experimentally from the other diffuse side of the peak.[11,15] Hence, the isotherm relating a and c may be found using eq 1.

This method is less accurate than frontal analysis, as all kinetic factors and gas-phase volume changes due to vapor adsorption are ignored. However, it has the advantage of being much faster and simpler experimentally, and if conditions are chosen to minimize errors the resultant adsorption isotherms agree with those obtained by static measurements.[11]

Experimental Section

A Microtek Model DSS-162 gas chromatograph with dual hydrogen flame detectors was equipped with accurate flow controls and pressure gauges on the carrier gas inlets. Retention times were calculated from a chart recorder trace of the elution chromatograms and were corrected for column "dead volume." The volume flow rate of nitrogen carrier gas was measured using a soap bubble flowmeter and was corrected for gas compressibility. The gas chromatographic columns described in Table I were prepared either by sieving beads of commercial polymers or by evaporation of a polymer solution in contact with gently stirred glass beads. Relatively large spherical beads (35/50 or 60/80 mesh) were used rather than substrates with higher specific surface areas in order to minimize the kinetic factors which cause peak broadening. The spherical bead packings facilitated the estimation of the geometric surface area in a column, and also allowed the operation of the columns with a small pressure drop (~1 psi) along the column, thus minimizing the corrections necessary for gas compressibility.

The polymers were obtained from the sources indicated in Table I; the number-average molecular weights of the poly(methyl methacrylate) and poly(vinyl acetate) samples were obtained by membrane osmometry in *n*-butyl acetate. After packing, the chromatographic columns were held at 60° in a stream of nitrogen for several hours to remove any volatile impurities from the polymer. Analytical standards (Poly Science Corp., Qualkits) were

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TABLE I
GAS CHROMATOGRAPHIC COLUMNS

Column[a]	Length, m, 0.25-in. o.d. tube	Polymer	Weight, g	Geometric area, cm^2	BET area (n-decane), cm^2
A	1.2	Poly(methyl methacrylate)[b]	15.87	2540	2460
B	0.6	Poly(methyl methacrylate)[b]	7.73	1240	1300
C	0.6	Poly(styrene-*co*-divinylbenzene)[c]	7.04	2020	3690
D	1.0	Polystyrene[d]	0.157[g]	2060	1930
E	1.5	Poly(vinyl acetate)[e]	0.104[g]	4860	3860
F	1.2	Glass beads	33.3	2460	
G	1.0	Polyethylene[f]	0.163[g]	3170	

[a] Columns C, E, and G, sieved 60/80 mesh; A, B, D, and F, sieved 35/50 mesh. [b] Fisher Scientific, $\overline{M}_n$ = 48,000. [c] Dow Chemical, 8% cross-linked. [d] Pressure Chemical, molecular weight 51,000. [e] BDH Chemicals, $\overline{M}_n$ 42,000. [f] Tennessee Eastman, Tenite 3310. [g] Polymer coated onto glass beads.

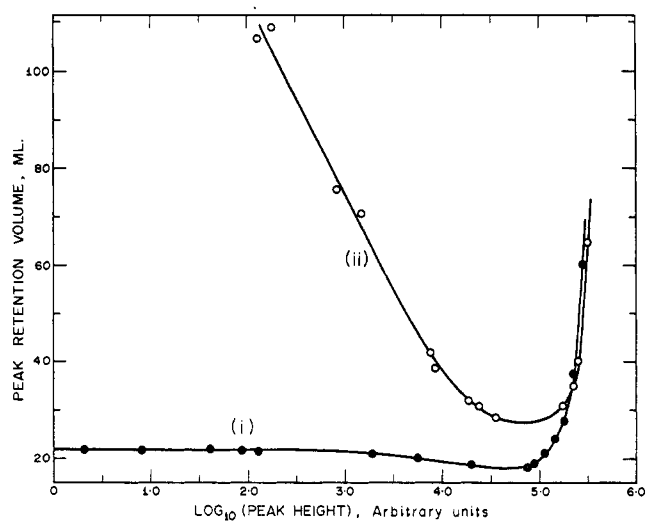

Figure 1. The effect of sample size on peak retention volumes at 25° for n-decane on (i) poly(methyl methacrylate), column A, and (ii) poly(styrene-*co*-divinylbenzene), column C. A peak height of 10^5 arbitrary units corresponds to 0.02 μl of n-decane.

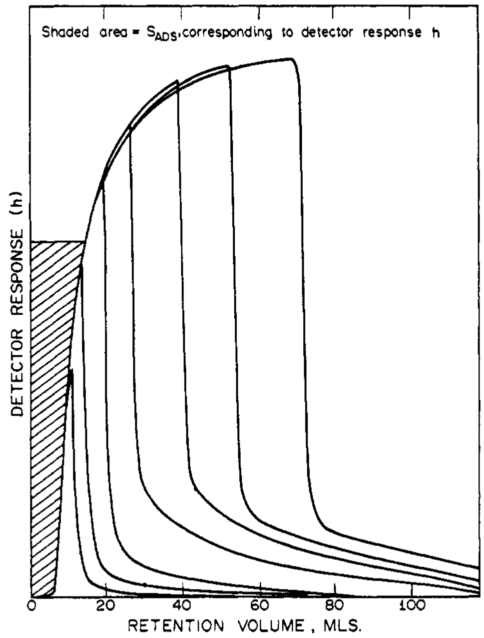

Figure 2. Chromatographic peak shapes for larger injections of n-decane on poly(methyl methacrylate) beads, column B, at 25°. Injection sizes, ~1.0, 0.7, 0.5, 0.3, 0.15, 0.06, 0.03 μl.

used as sorbate compounds. The sorption data were obtained gravimetrically; pressed films of polymer, after a thermal treatment comparable to that given to the gas chromatographic columns, were suspended in air saturated with n-decane vapor at 23.5° and the weight gain was measured using a Cahn Electrobalance.

Results and Discussion

The shape of the distribution isotherms is reflected by the effect of the size of the injected probe sample on its gas chromatographic retention volume. Figure 1 illustrates qualitatively two distinct types of behavior found for n-decane probe on (i) poly(methyl methacrylate) and (ii) polystyrene.

The increase in peak retention volume with injection size shown on both polymers for large injections (*i.e.*, log (peak height) > 5) is considered first. The shape of the experimental elution peaks changed as the amount of n-decane was increased; the front profiles became increasingly diffuse but fell on a common curve, while the rear profiles remained almost vertical. This is shown for decane on poly(MMA) in Figure 2. The conditions required for the calculation of isotherms from elution chromatograms were thus obeyed for this system, and eq 1 may be applied to obtain the amount of n-decane sorbed on the column as a function of its partial pressure in the following simple manner.[10] The partial pressure of the n-decane vapor entering the gas chromatographic detector may be related to the experimental chromatogram by

$$p = (m_{cal} q RT / S_{cal} \dot{V}) h \qquad (2)$$

where p = the partial pressure of the eluting n-decane at column temperature T°K corresponding to recorder pen deflection h, S_{cal} = the calibration peak area on the recorder chart for an injection of m_{cal} moles of n-decane, q = the recorder chart speed, R = the gas constant, and $\dot{V}$ = the carrier gas volume flow rate at column temperature. The amount of decane sorbed corresponding to this partial pressure p is given by

$$a = m_{cal} S_{ads} / m S_{cal} \qquad (3)$$

where a = the amount of decane sorbed (per unit weight of sorbent), m = the mass of the sorbent, and S_{ads} = the chart area bounded by the diffuse profile of the chromatogram, carrier gas front, and height h (see Figure 2). By measuring areas S_{ads} corresponding to different values of h, the isotherm relating a and p may be calculated using eq 2 and 3.

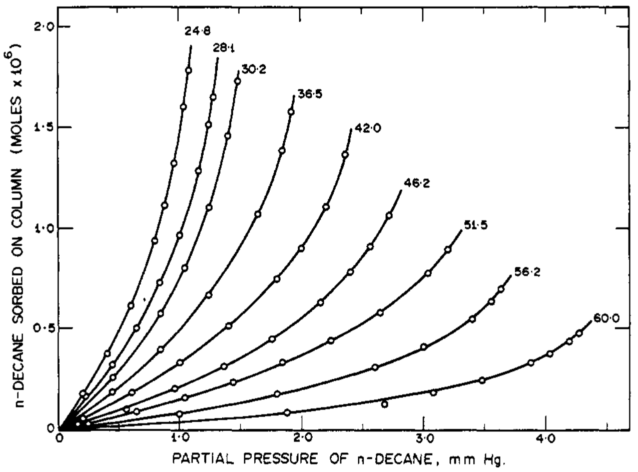

Figure 3. Isotherms at the indicated temperatures for *n*-decane on poly(methyl methacrylate) beads, column A.

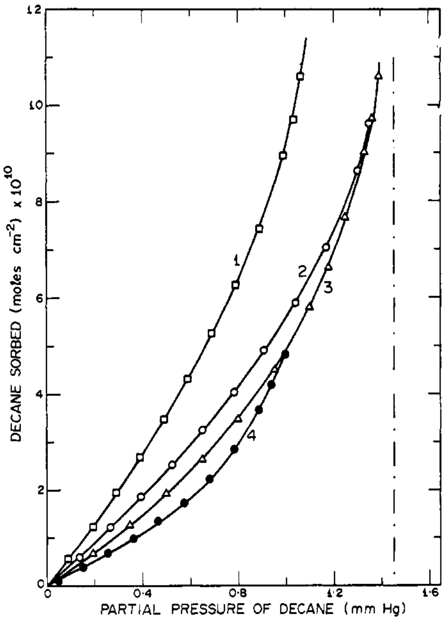

Figure 4. Sorption isotherms for higher *n*-decane concentrations on some polymers at 25°: (1) poly(styrene-*co*-divinylbenzene) beads, column C; (2) polystyrene-coated glass beads, column D; (3) poly(methyl methacrylate) beads, column B; (4) poly(vinyl acetate)-coated glass beads, column E.

A series of isotherms for *n*-decane on poly(methyl methacrylate) at a number of temperatures obtained by this method is shown in Figure 3. The isotherms correspond to type III in Brunauer's classification,[16] which has been ascribed to multilayer adsorption, where the heat of adsorption is equal to or less than the heat of liquefaction of the adsorbate. As the amount of adsorbate on the surface is increased, the partial pressure of its vapor should as a limit approach the vapor pressure of the pure adsorbate at the temperature in question. This was found to be the case for *n*-decane on poly(methyl methacrylate) and was confirmed by determining the sorption isotherms at 25° for *n*-decane on polystyrene-coated glass beads, poly(styrene-*co*-divinylbenzene) beads, and poly(vinyl acetate)-coated glass beads (Figure 4). The adsorption per unit geometric area for all but the poly(styrene-*co*-divinylbenzene) beads was very similar for a given partial pressure of decane, and the vapor pressure of pure decane was approached asymptotically. (The exception may be due to readily accessible internal pore space for the cross-linked copolymer; see Table I.) Thus, for the sorption of *n*-decane on these glassy polymers, the shape of the isotherm at high coverages is governed primarily by surface saturation.

Returning to the two distinct types of behavior at low *n*-decane concentrations shown in Figure 1, the peak retention volumes on poly(methyl methacrylate) remained almost constant for injected sample sizes ranging over four orders of magnitude. The peaks were sharp, with only slight tailing. Care was, however, necessary in measuring retention volumes, as they were increased markedly by previous large injections of decane, so that small injections were performed first and adequate time was allowed between injections. It is therefore reasonable to assume that in this region the distribution isotherm is effectively linear and that thermodynamic information may properly be derived from peak retention data on poly(methyl methacrylate) beads.

On both poly(styrene-*co*-divinylbenzene) beads and on polystyrene-coated glass beads, the peak retention times for *n*-decane increase markedly with decreasing injection size (Figure 1, curve ii). The peaks display a diffuse rear profile and broaden so much with decreasing sample size that they become almost indistinguishable from the base line at very small injection sizes. This behavior would be expected if the sorption isotherm for *n*-decane on polystyrene is not linear but remains concave toward the pressure axis to the lowest accessible concentrations, suggesting a nonhomogeneous substrate, with stronger sorption occurring as surface coverage decreases. However, quantitative calculation of the isotherm shape is not possible from these elution chromatograms because the diffuse rear profiles of the peaks for different injection sizes do not fall on a common curve. This implies that the column is not functioning close to equilibrium conditions, but that some kinetic process is causing peak broadening.

The most obvious kinetic process which might lead to the observed results involves the partial penetration of the probe into the bulk of the polymer. Sorption of organic vapors into the bulk of glassy polymers is well known, although the process is much slower and more complex than sorption into polymers above their glass-transition temperature.[17] To illustrate the magnitude of this sorption, some gravimetric experiments on polymer films suspended in saturated decane vapor at room temperature were performed. Figure 5 indicates the comparative rate of sorption of *n*-decane on glassy polystyrene and poly(methyl methacrylate) and also on low-density polyethylene, a polymer composed of about 45% amorphous material. These data show that even on the time scale of the chromatographic experiments, sufficient absorption may occur to alter the peak shape. Quantitative treatment of the effect is difficult, owing to the complex time dependence of the surface concentration in the chromatographic column and to the number of variables governing the rate of diffusion of penetrants in glassy polymers.[17] Quantitatively, slow bulk sorption and desorption would be expected to produce a marked skewing and tailing of the chromatographic peaks, superimposed on the diffuse rear profile resulting from the nonlinearity of the sorption isotherm. Thus, at low concentrations the rear profiles would no longer be superimposable, as was found on polystyrene.

This explanation for the experimental results on polystyrene

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TABLE II

ENTHALPIES OF DESORPTION ON POLY(METHYL METHACRYLATE), COLUMN A, BETWEEN 25 AND 60°

Sorbate	ΔH_v,[a] kcal/mol	$(\Delta H_s)_{a,0}$,[b] kcal/mol	ΔH_s at indicated coverage, kcal/mol[c]: 0.95×10^{-6} mol m^{-2}	1.7×10^{-6} mol m^{-2}	2.4×10^{-6} mol m^{-2}
n-Decane	12.1	12.0 ± 0.2	12.6 ± 0.5	11.7 ± 0.5	~11
n-Hexyl alcohol	15.7	12.8 ± 0.2			

[a] Calculated from vapor pressure data (ref 19). [b] Overall enthalpy of desorption at low surface coverage, from log V_g *vs.* $1/T$ data. [c] Calculated from temperature dependence of isotherms.

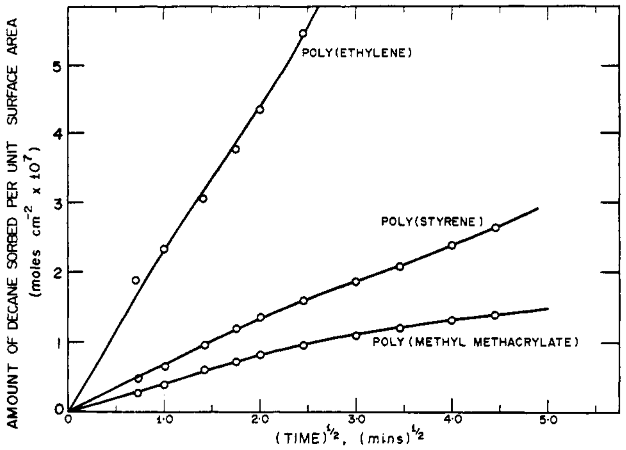

Figure 5. Initial sorption of *n*-decane at its saturation vapor pressure on polymers at 23.5°.

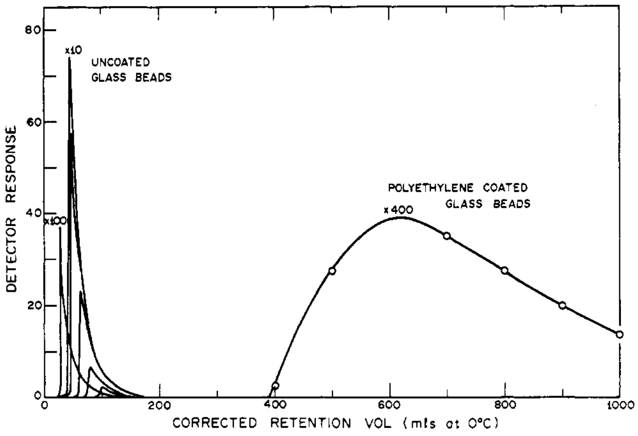

Figure 6. Typical gas chromatograms for *n*-decane on glass beads, column F, and in polyethylene, column G, at 23°.

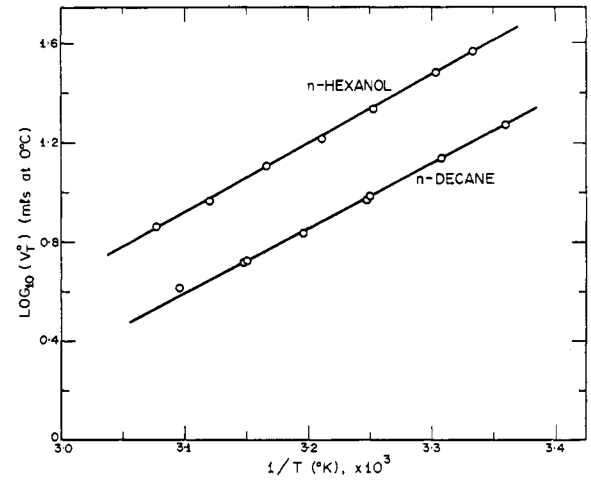

Figure 7. Arrhenius plots of retention volumes for *n*-becane and *n*-hexane on poly(methyl methacrylate) beads, column A.

is supported by a comparison of the gas chromatographic retention of *n*-decane on polyethylene, where bulk sorption is rapid (Figure 5), and on uncoated glass beads, where it is impossible. In the latter case, at low *n*-decane concentrations, the diffuse rear slopes are almost superimposable (Figure 6), indicating that whatever factor caused the tailing on polystyrene is absent on glass. As experimental factors such as longitudinal diffusion in the gas phase, column geometry, and sample input distribution are common to all the experiments reported here, the most reasonable remaining possibility is nonequilibrium bulk sorption, which is not possible with the glass beads. On the other hand, when *n*-decane is injected onto a column containing polyethylene, an extremely broad retention peak (Figure 6) is eluted at retention volumes nearly two orders of magnitude greater than from an identical column containing the same weight of polystyrene. The retention volume is in accord with an extrapolation of similar data,[4] where the predominant retention mechanism is undoubtedly bulk sorption in the amorphous phase. Thus, with polyethylene, the rate of sorption into the bulk is just fast enough to allow equilibrium to be established in the time scale of the chromatographic experiment. The much slower rate of sorption of *n*-decane into polystyrene means that surface rather than bulk interactions must be the predominant retention mode; this conclusion is supported by the similar retention properties of the column containing solid polymer beads and the column containing a much smaller weight of polymer coated onto glass beads (see Figure 4). However, the rate of sorption appears to be sufficient to distort the chromatographic peaks on polystyrene and thus prevent the calculation of isotherms directly from chromatographic peak shape at low *n*-decane concentrations.

Heat of Adsorption. When the gas chromatographic retention volumes for a polymer–probe system are independent of the size of the probe sample at low sample sizes, the heat of sorption may be readily determined from the change in retention volume with temperature[11,12]

$$\frac{\partial \ln V_g}{\partial(1/T)} = \frac{\partial \ln (V_s/T)}{\partial(1/T)} = \Delta H_s/R = (\Delta H_v - h_e)/R \tag{4}$$

where V_g = the specific retention volume measured at 0°; V_s = the retention volume per unit surface area, measured at column temperature T°K; ΔH_s = the overall heat of desorption from the surface into the vapor phase; ΔH_v = the latent heat of evaporation of the probe molecule; and h_e = the excess enthalpy of sorption of the liquid probe onto the polymer. The retention volumes for small injections of *n*-decane on poly(methyl methacrylate) were measured between 25 and 60°. A plot of the logarithm of the retention volume against reciprocal temperature was linear (Figure 7), enabling ΔH_s to be determined at effectively zero surface coverage (Table II).

For this system, ΔH_s was found to be the same within experimental error as ΔH_v for n-decane. Thus, any specific interaction between the hydrocarbon probe and the polymer surface must be very small.

When retention volumes depend on sample size because of nonlinear distribution isotherms, the enthalpies of sorption for different surface coverages may in principle be found from isotherms measured at different temperatures. As an example the isotherms for n-decane on poly(methyl methacrylate) at high coverages (Figure 3) were used to calculate enthalpies for different amounts of sorbed decane using

$$(\Delta H_s)_a = -R\left[\frac{\partial \ln p}{\partial(1/T)}\right]_a$$

where p is the partial pressure of n-decane in the vapor phase, and the subscript a indicates quantities measured at a given value of a, the amount of n-decane sorbed on the surface. The range of coverage accessible by this method over a reasonable temperature interval is rather restricted, and the apparent change in ΔH_s with coverage (Table II) may result from the approximate nature of the calculated isotherms. The average value does, however, appear to be close to the latent heat of evaporation of n-decane, as would be expected for a multilayer on the polymer surface.

As a further example, a system was investigated where specific probe–probe and probe–polymer interactions are possible. When n-hexyl alcohol was used as a probe on poly(methyl methacrylate), the peak shapes at very low concentrations showed considerable tailing, but the peak retention times were relatively constant over a range of injection sizes. In this range, a plot of the logarithms of the peak retention volumes against reciprocal temperature gave a good straight line (Figure 7). The overall heat of desorption, ΔH_s, calculated from this line was considerably smaller than the equivalent heat of evaporation, ΔH_v, for pure n-hexyl alcohol (Table II). The resultant positive value for h_e of 2.9 kcal per mole of n-hexyl alcohol is ascribed to the greater enthalpy required for vaporization from the pure liquid state compared to desorption from the polymer surface. In the pure liquid, strong hydrogen bonding between the hydroxyl groups of the alkanol occurs, but for the small amounts of probe sorbed in this gas chromatographic experiment, the alkanol–alkanol interactions are unimportant, and only alkanol–polymer interactions are operative. Enthalpy data for alkanols on graphitized carbon black have been attributed to this effect.[18] An accurate knowledge of the enthalpy of hydrogen bond formation is therefore necessary to determine the enthalpy of the specific polymer–probe interactions. If, however, a value of 4.8 kcal/mol may be assumed for alkanol hydrogen bond formation,[18] then approximately $(4.8 - h_e) = 1.9$ kcal/mol remains as the enthalpy of polymer–n-hexyl alcohol interaction at low surface coverage.

For higher concentrations of n-hexyl alcohol on polymethyl methacrylate), the "isotherms" calculated from gas chromatographic peaks showed anomalous behavior. (For example, severe tailing occurred on the rear slope of the chromatographic peaks, and the vapor pressures[19] approached asymptotically by the isotherms at high coverage were only half the expected values for pure liquid n-hexyl alcohol at the corresponding temperatures.) These results were consistent with bulk sorption of the alkanol, and thus no enthalpy terms could be calculated for surface adsorption at high coverage with this system.

Measurement of Surface Areas. Gas chromatographic measurements of the specific surface area of solids have been performed by three different methods. While not strictly a chromatographic procedure, the thermal desorption method[20] has been widely applied, in some cases to polymeric substrates.[21] The area is determined from the amount of nitrogen sorbed at liquid nitrogen temperatures and is usually applied to materials with relatively high specific surface areas.

Secondly, in cases where the adsorption isotherm is linear and surface adsorption is the only retention mechanism, the measured retention volume is linearly related to the surface area for a given adsorbate, adsorbent, and temperature. Thus by measuring the retention volume for small injections of n-decane on a poly(methyl methacrylate) column of known surface area, the retention volume per unit surface area at a given temperature may be calculated. For example, by interpolation of the data shown in Figure 7, the retention volume on column A is 19.9 ml measured at 25°, giving a surface retention volume of 80 ml m^{-2} for n-decane on poly(methyl methacrylate). Hence, the surface area of other samples of poly(methyl methacrylate) may be readily obtained by measuring the retention volume of n-decane on a suitable column of the material. When applicable, this is the most convenient method for determining surface areas, but it requires a linear distribution isotherm for the probe on the polymer surface and the absence of bulk sorption effects.

A third method involves calculation of the isotherm shape from chromatographic data for relatively high coverage of a suitable probe and applying the BET approach[16] to deduce the specific area from the isotherm.

A two-parameter BET equation was used in the form

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + \frac{C-1}{v_m C}x$$

where $x = p/p_0$, $p =$ the vapor pressure of the adsorbate over the surface, $p_0 =$ the saturation vapor pressure of the pure liquid adsorbate, $v =$ the volume of the adsorbate on the surface, $v_m =$ the volume of adsorbate on the surface corresponding to monolayer coverage, and C is a constant (for $0.05 < x < 0.35$). Using values for v and x from the experimental isotherms, $x/v(1 - x)$ was plotted as a function of x, and v_m was calculated from the slope and intercept of the resultant straight line. Thus, if the surface area covered by the probe molecule is known, then the area of the surface in the chromatographic column may be obtained. The surface area occupied by an n-decane molecule on a polymer surface where only weak interactions are expected may be extrapolated approximately from Kiselev's data for a series of n-alkanes on graphitized carbon black,[22] where somewhat similar surface species are to be expected. Taking 70 Å^2 as this area, and estimating the point of monolayer formation from the slope and intercept of BET plots for values of p/p_0 between 0.05 and 0.35, the values obtained for surface areas (Table I) were comparable with the geometric surface areas, except again in the case of the poly(styrene-*co*-divinylbenzene) copolymer.

Conclusion

Under appropriate conditions, simple elution techniques of gas-adsorption chromatography may be applied to polymeric

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substrates to obtain sorption isotherms and hence to determine surface areas and enthalpies of adsorption. A primary requisite for this application is that bulk sorption into the polymer does not contribute to the retention of the adsorbate on the gas chromatographic column. Thus, only compounds having little tendency to dissolve in or swell the polymer in the time scale of the gas chromatographic experiment are useful as adsorbates. (Bulk sorption may also be reduced by working at column temperatures well below the glass-transition temperature of the polymer under study, where the rate of penetration is slower.)

Columns of relatively low internal surface area are necessary to avoid kinetic effects on peak shape which would invalidate the method used to calculate adsorption isotherms. In view of the low column area, and the resultant use of large, relatively nonvolatile adsorbate compounds, the agreement between the geometric surface areas of the polymers and the areas measured by the BET treatment of experimental isotherms is satisfactory. The use of relative peak retention volumes, measured at effectively zero coverage, provides an alternative and more rapid method of surface area determination. In this case, no restriction on the surface area of the column is necessary; in fact, as the specific surface area of the polymer is increased, the linear distribution region becomes more accessible and measurement of retention values becomes more accurate.

When a linear distribution region is accessible at low adsorbate concentrations, enthalpy data on adsorbate–polymer interactions may be readily derived from the variation in peak retention volumes with temperature. However, the results for *n*-hexyl alcohol on poly(methyl methacrylate) show that due allowance must be made for possible adsorbate–adsorbate interactions. When the distribution isotherms are nonlinear, the temperature dependence of the isotherm shape should in principle enable adsorption enthalpies to be calculated as a function of surface coverage. However, the accuracy of adsorption enthalpies calculated by this method from nonlinear isotherms appears unsatisfactory.

In general, a significant amount of information on the properties of polymer surfaces may be obtained by simple and rapid gas chromatographic experiments.

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Molecular Weight–Intrinsic Viscosity Relationships for Phenol–Formaldehyde Novolak Resins[1a]

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ABSTRACT: Intrinsic viscosity and number-average molecular weight data have been determined for fractionated acid-catalyzed linear phenol–formaldehyde novolak resins. The Mark–Houwink expressions for the fractionated phenol–formaldehyde polymer in acetone, DMF, and 1 *N* NaOH at 25° were found to be $[\eta] = (1.90 \times 10^{-3})M^{0.47}$, $(1.80 \times 10^{-3})M^{0.51}$, and $(1.66 \times 10^{-3})M^{0.48}$, respectively, for a molecular weight range of 1000–8000. The log $[\eta]$–log M plot curves upward below 1000, similar to a number of other low molecular weight polymers which have recently been studied. The unperturbed end-to-end chain dimensions were estimated by the Flory–Fox method to be $0.88M^{1/2}$ Å. For the unfractionated parent polymer, a molecular weight ratio M_w/M_n of approximately 2.3 was found, with M_w and M_n in the region of 2100 and 900, respectively. Solvent behavior in formamide, ethyl acetate, methanol, and NaOH showed interesting effects on the Mark–Houwink data, not only through curve displacement, but also by shifting the position of the low molecular break in the curve. Variation in the Mark–Houwink parameter *a* from 0.51 in DMF to 0.24 in formamide is examined in terms of chain coil compactness.

Polymers formed by the reaction of phenol and formaldehyde under varied mole ratios and either acid or base catalyst conditions produce interesting and useful materials. The materials which are described here are called novolaks, since they are prepared with a mole ratio of phenol to formaldehyde greater than one and under acid conditions. A typical structure is shown in Figure 1. The linkages are distributed between ortho and para positions,[2] and form what might be considered a flexible linear polymer system. On the other hand, if the polymerization is carried out in a basic medium with the phenol to formaldehyde mole ratio less than one, resoles are formed that are branched and have reactive methylol end groups.

This viscosity–molecular weight study on linear novolak structures was undertaken to formulate a model which would be useful in interpreting properties such as stiffness, branching, and molecular weight distribution in the more complicated resole structures.[3] This system also proves to be a novel one in which to study the dilute-solution properties of low molecular weight materials which have drawn attention recently.[4–6] Present theory predicts that viscosities should decrease rapidly as low molecular weights are approached, but this is not generally observed experimentally.

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(1) (a) Part of the material was presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **11**, 1101 (1970). (b) Pacific Lutheran University. (c) Reichhold Chemicals.

(2) (a) A. A. K. Whitehouse, E. G. K. Pritchertt, and G. Barnett, "Phenolic Resins," Elsevier, New York, N. Y., 1968; (b) W. Martin, "The Chemistry of Phenolic Resins," Wiley, New York, N. Y., 1956, pp 107–109.

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