Inverse Gas Chromatography of Glassy Polymer Surfaces

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ABSTRACT: Broad peaks are often observed when inverse gas chromatography (IGC) is used below the glass transition temperature to determine adsorption thermodynamics at polymer surfaces. Peak first moments for polar and nonpolar adsorbates on poly(methyl methacrylate), polystyrene, and Illinois No. 6 coal do not shift and the peaks do not broaden with increasing injection amount, demonstrating that peak broadening does not result from isotherm nonlinearity. A comparison of diffusion coefficients and IGC retention times shows that equilibrium diffusion through the polymer is not responsible for the peak broadening. Changes in flow rate have no effect on the retention time, demonstrating that nonequilibrium diffusion is not responsible for the peak broadening. No matter which mechanism is responsible for the peak broadening, the retention volumes are sensitive to interactions at the polymer surface.

Introduction

Inverse gas chromatography (IGC) is used routinely to determine interaction energies of polar and nonpolar molecules with polymers.[1-9] Above the glass-to-rubber transition temperature (T_g), the technique is sensitive to properties of the *bulk* polymer.[10] Below T_g, the technique has been used to determine interactions at polymer *surfaces*.[2-9,11] Broad peaks are often observed below T_g.[4,7-9,12] Broad peaks often result when injected molecules diffuse into the stationary phase bulk.[13] If diffusion into the bulk polymer is occurring below T_g, the technique is not sensitive to surface interactions only, bringing into doubt the use of IGC to obtain polymer surface thermodynamics. Because we wanted to use IGC to determine adsorption thermodynamics for molecules interacting with the surface of the complex macromolecular solid, coal, it was necessary to determine if the technique is sensitive to surface interactions *only*.[14] Others have studied the behavior of the retention volumes, but the behavior of the peak widths below T_g has not been experimentally demonstrated.[4,7-10,15] We studied peak broadening for several adsorbates on two glassy polymers and a coal.

Two important parameters in IGC are the retention volume and the peak width or peak broadening. At temperatures above and near T_g, the origin of IGC retention volumes and peak broadening are well understood.[10,16-21] Because injected molecules diffuse rapidly through the polymer above T_g, the retention volumes represent thermodynamic interactions of injected molecules with the bulk polymer.[10,16,18,20] The flow rate dependence of the peak widths has been used to determine diffusion coefficients in the polymer bulk.[22-26] At temperatures within about 50 deg of T_g, nonequilibrium diffusion, characterized by a kinetically-controlled (flow rate-dependent) retention volume, sets in.[16-21,27] The retention volumes are characteristic of the distance the injected molecules travel into the bulk, and they cannot be used to determine equilibrium thermodynamic properties. The peak width and retention volume behavior in this regime are complex and depend on several factors including the nature of the injected molecules, the polymer thickness, and the polymer crystallinity.[16-18,21,28]

For IGC on glassy polymers at temperatures below T_g, it has been demonstrated that for sufficiently small injection sizes the requirements of linear chromatography are met, the retention volumes do not shift with flow velocity, and they are sensitive to the polymer surfaces.[4-9,18,27,29-31] IGC peaks below T_g are non-Gaussian, and first moments should be used to calculate retention volumes.[32] When peak broadening is caused by nonlinear chromatography, the retention volumes shift and the peaks broaden with increasing injection amount because a range of sites of different energies is sampled, strongest first.[13] Below T_g, retention volumes were constant with injection amount for polar and nonpolar adsorbates on polycarbonate, for alkanes on Kevlar, for alkanes and chloromethanes on polymer-coated glass beads, for alkanes on a polyester, and for various adsorbates on cellulose.[4-9,29] This is taken as evidence that, at sufficiently low injection amounts, linear chromatography holds for these systems.[4-9,29] Injection size-dependent peaks were reported for tetrachloroethane, butyl acetate, and dioxane on Kevlar at unknown injection sizes and for ether and acetone on polymer-coated glass beads at injection sizes below 0.1 mL.[7,8] At larger injection sizes, adsorption isotherms have been determined from IGC peaks for adsorbates on polymers below T_g.[16,29] Only anti-Langmuir type isotherms corresponding to increased adsorbate–adsorbate interaction energies at higher injection amounts were observed for *n*-decane on poly(methyl methacrylate) (PMMA), and for *n*-decane, dioxane, and *n*-alcohols on cellulose.[16,29] Retention volumes below T_g were shown to be independent of column flow velocity for *n*-hexadecane on polystyrene (PS), for *n*-octane and carbon tetrachloride on poly(vinyl acetate), and for alkanes on cellulose, demonstrating that these retention volumes were not affected by nonequilibrium diffusion into the polymer.[18,27,30] Braun and Guillet showed that accessible surface areas calculated from the retention volumes were similar to the specific surface area for *n*-hexadecane on PS, demonstrating that the retention volumes are sensitive to the polymer surfaces.[18] Glass and Larsen showed that retention volumes for alkanes on Illinois No. 6 coal depend on the coal particle size, demonstrating that the retention volumes are sensitive to the external surface of the coal.[31] These data provide evidence that linear chromatography holds at sufficiently low injection amounts and that nonequilibrium diffusion is not affecting the retention volumes below T_g. Studies of the flow rate and injection size dependence of the peak broadening are needed to provide further evidence that surface properties *only* are contributing to IGC below T_g.

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Peak broadening below T_g has not been studied in detail, but several different explanations have been offered for the broad peaks.[10,12,15,19,33] It was thought that diffusion into the polymer bulk was occurring so that bulk interactions were in part responsible.[10,12,15] It was thought that "soluble" molecules diffused into the bulk polymer and reported both bulk and surface properties, while insoluble molecules did not diffuse into the polymer and as a result reported only surface properties.[10,15] However, Braun and Guillet stated that the solubility does not determine the tendency to diffuse into the bulk at temperatures near T_g.[19] It was also thought that IGC peaks below T_g might result from a combination of nonlinear and nonideal chromatographic effects.[12] If both of these effects were operating simultaneously, it would be difficult if not impossible to extract meaningful information from the IGC peaks.[34] Katz and Gray thought that the broad peaks they observed for *n*-alkanes on cellophane were probably caused by diffusion in the gas phase.[33]

The origin of the peak broadening below T_g remains uncertain. Studies reported here of the flow rate and injection size dependence of IGC peaks for adsorbates on PS, PMMA, and Illinois No. 6 coal show that the broad peaks are not caused by diffusion into the bulk.

Experimental Section

Experiments were conducted using the apparatus described previously.[31] The GC was a Hewlett Packard 5890 with a flame ionization detector. Briefly, the adsorbate gas of interest was admitted to a vacuum manifold and then to a Valco injection valve (0.015- or 0.100-mL sample loop). The pressure of gas in the injection loop was determined with a Baratron (MKS Instruments) gauge located in the vacuum manifold. This allowed injection of known amounts of gas onto the column.

Gases were 99% purity or better. Liquids were obtained from Aldrich in "sure-seal" bottles and subjected to at least three freeze–pump–thaw cycles before being introduced into the vacuum manifold at pressures below their vapor pressures.

PMMA and PS beads were obtained from Polysciences, Inc. PMMA was used as received (200-μm beads) or was coated onto Chromosorb W AW 80/100 mesh (Supelco, Inc.) by evaporation from methylene chloride. PMMA beads (4.09 g) were packed into a $^1/_8$-in.-o.d., 2.1-mm-i.d. stainless steel column 154.2 cm long. Chromosorb (1.76 g) containing 4.13% weight loading PMMA was packed into a $^1/_8$-in.-o.d., 2.1-mm-i.d. stainless steel column 134.9 cm in length. PS beads were sieved to 60/40 mesh, and 3.37 g was packed into a $^1/_8$-in.-o.d., 2.1-mm.i.d. stainless steel column 154.3 cm in length. The columns were heated at temperatures slightly above T_g (at 110 °C for PMMA and at 105 °C for PS) overnight in helium before each day's experiments.

Argonne premium Illinois No. 6 coal was sieved to 60/70 mesh, and 3.95 g was packed into a $^1/_8$-in.-o.d., 2.1-mm-i.d. stainless steel column 153.5 cm in length. The column was heated at 150 °C in helium for 2 weeks and overnight before each day's experiments. Extracted coal was prepared by extracting Illinois No. 6 coal of 40/60 mesh particle size in a Soxhlet extractor for several days in tetrahydrofuran (THF). The coal was dried in a vacuum oven at 110 °C overnight. The coal (3.88 g) was packed into a stainless steel column 152.9 cm long, $^1/_8$-in. o.d., and 2.1-mm i.d. The column was heated in helium at 250 °C for 2 weeks and overnight before each day's experiments.

For PMMA and PS, injections were made over the temperature range 30–55 °C, with injector and detector temperatures at 70 °C. For coal, injections were made over the temperature range 30–150 °C with injector and detector temperatures at 150–180 °C. The temperature of the chromatograph oven was accurate to ±0.1 deg and was unchanged within 0.2 deg of the recorded temperature over different parts of the oven.

Flow rates, determined from the GC mass flow control readout and checked periodically with a bubble meter, ranged from 5 to 40 mL/min. They were corrected for water vapor. The column pressure drop was measured with a pressure transducer (Omega Engineering, Inc.) on the column inlet and a barometer in the ambient atmosphere. Typical pressure drops were 1–2 atm. Retention volumes were corrected using the pressure drop correction term j.[35] Average linear flow velocities, $\bar{u}$, were calculated from the column length, l, and the dead time, t_m ($\bar{u} = jl/t_m$).[36] Column dead times were determined using columns containing glass beads of the same average particle diameter as the polymer and coal columns.

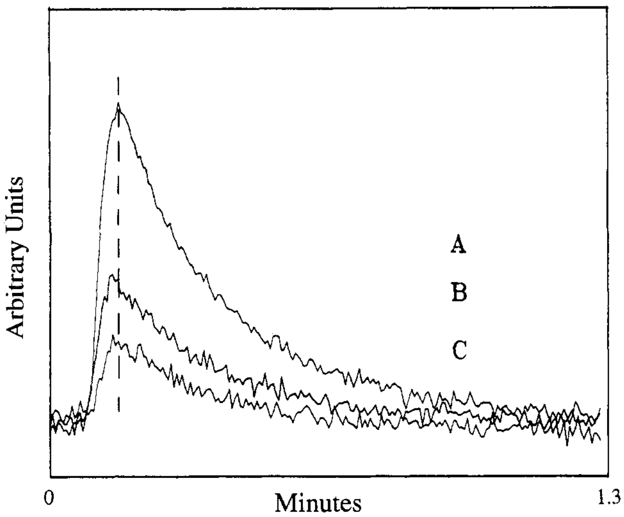

Figure 1. IGC peaks for different injection amounts of *n*-pentane on polystyrene: (A) 8.0 × 10^{-6} μmol; (B) 4.0 × 10^{-6} μmol; (C) 2.4 × 10^{-6} μmol. Column temperature = 33 °C, flow rate = 7.2 mL/min.

Data from the GC were sent via a modified 16-bit Keithley A/D board to a PC. Points were collected at a rate of one per second and input to LabCalc software (Galactic Industries, Corp.). The retention volumes of the peaks were calculated from the first moments which were determined by integrating the peaks. Peak standard deviations were measured at 0.607 times the height (at this height, the standard deviation in time units, $\sigma_{(t)}$, equals half the peak width).[37]

Results and Discussion

Figure 1 shows IGC peaks for *n*-pentane on PS. These data are typical of those used to determine retention volumes for polar and nonpolar adsorbates on PS, PMMA, and Illinois No. 6 coal at temperatures below the glass transition temperature. The first moments of the peaks in this regime remained constant over a range of about a factor of 5 in injection amount. Retention volumes that are independent of injection amount were observed by others for polar and nonpolar adsorbates on different polymers below T_g.[4–9,29] These observations demonstrate that at sufficiently small injection sizes, the linear region of the adsorption isotherm is being sampled. Linear chromatography holds. The broad peaks in this regime (Figure 1) cannot be caused by nonlinear chromatography. Assuming close packing of *n*-pentane on the PS surface, the injection sizes in Figure 1 correspond to about 0.1% surface coverage of the polymer in the column. If the adsorbate is occupying 1/100th of the column (~1.5 cm), this corresponds to 10% surface coverage. The distribution of adsorbate on the column is not known, so the true surface concentration cannot be determined.

At higher injection amounts, peak tailing was observed. See Figure 2. Others have observed peak tailing below T_g for ethanol on Kevlar.[7] Because tails lead to increased first moments, tailed peaks cannot be used to determine retention volumes.[38] In order to stay below the tailing regime, and to obtain accurate first moments, very small injection sizes are required. We constructed a vacuum manifold to inject these small amounts of adsorbate onto the columns. The tailed peaks reported by others probably

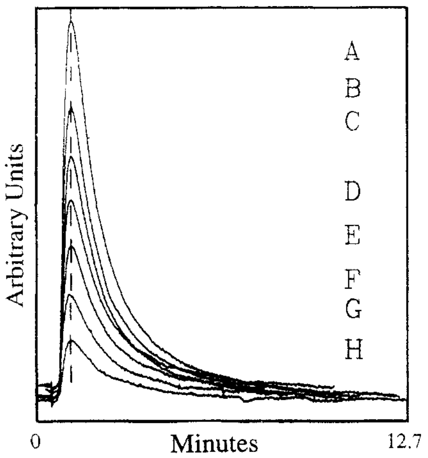

Figure 2. IGC peaks for different injection amounts of n-pentane on extracted Illinois No. 6 coal: (A) 2.2×10^{-4} μmol; (B) 1.7×10^{-4} μmol; (C) 1.4×10^{-4} μmol; (D) 1.2×10^{-4} μmol; (E) 1.0×10^{-4} μmol; (F) 5.4×10^{-5} μmol; (G) 2.5×10^{-5} μmol; (H) 1.5×10^{-5} μmol. Column temperature = 110 °C, flow rate = 30.4 mL/min.

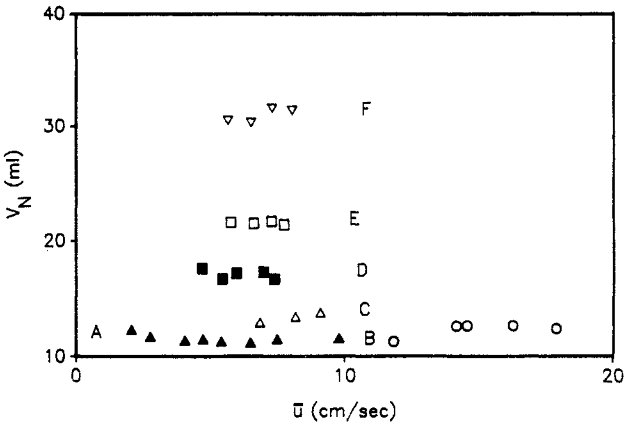

Figure 3. Plots of retention volume, V_N, vs linear flow velocity, $\bar{u}$, for alkanes on PMMA and Illinois No. 6 coal: (A) cyclopropane on Illinois No. 6 coal, 130 °C, ▲; (B) benzene on PMMA, 52 °C, ○; (C) n-pentane on Illinois No. 6 coal, 110 °C, △; (D) ethane on Illinois No. 6 coal, 80 °C , ■; (E) propane on Illinois No. 6 coal, 110 °C, □; (F) neopentane on Illinois No. 6 coal, 90 °C, ▽.

resulted because they could not inject sufficiently small amounts (syringes were used).

The tails observed by us and by others for IGC on glassy polymers may result from "slow kinetics".[39] The term "slow kinetics" is used to describe the existence of sites in the column ("slow sites") that have relatively long time constants.[39] These slow sites may be the result of limited diffusion into the bulk and/or very strong interactions with the stationary phase.[39,40] Giddings has used a two site model to describe the GC peaks that result from slow kinetics.[40] Briefly, the model is based on two distinct populations of sites, one with a relatively rapid time constant and the other with a very long time constant.[40] If a significant number of injected molecules occupy the slow sites, the GC peak will have a tail.[40] It is possible that on glassy polymers, some adsorbates, especially strongly interacting ones, may give tailed peaks. At larger injection sizes, we observed peak tailing that increased with increasing injection size for alkanes and polar adsorbates on PMMA, PS, and Illinois No. 6 coal. This behavior is in contrast to the behavior expected for a range of adsorption energies (nonlinear chromatography), where long retention times contribute less to the peak as the injection size is increased. As long as data are collected at small enough injection sizes, tailing does not contribute to the retention volumes.

If the peak broadening is caused by diffusion into the bulk polymer, then either equilibrium or nonequilibrium diffusion must be occurring during the experiments. Equilibrium diffusion may be due to either bulk diffusion or gas diffusion and is described by the van Deemter equation.[41] From the van Deemter equation, when peak broadening is caused by diffusion into the bulk, the peak width (measured as the standard deviation in volume units, σ_v) increases with increasing flow velocity.[41] When peak broadening is caused by diffusion in the gas phase, σ_v decreases with increasing flow velocity.[41] The van Deemter equation, however, assumes that the peak width is much less than the retention time, a condition which does not hold below T_g (Figures 1 and 2).[41] The van Deemter equation cannot be used to refute gas or bulk diffusion as peak broadening mechanisms below T_g. We use a different argument to show that diffusion into the polymer is not responsible for peak broadening below T_g.

If equilibrium diffusion is occurring, then the adsorbates must diffuse through the entire polymer during the experiment. Table I shows retention times for alkanes on PS, PMMA, and Illinois No. 6 coal along with the diffusion coefficients determined from static sorption experiments for the same systems.[42,43] The average diffusion distances, $\langle x \rangle$, were calculated using Fick's second law, $\langle x \rangle = 2\,(Dt/\pi)^{1/2}$ where D is the diffusion coefficient and t is the diffusion time (set equal to the IGC retention time).[44] The values of $\langle x \rangle$ in Table I are therefore upper limits for the distance that the injected molecules can diffuse into the polymer during our IGC experiments. It is seen from the table that the maximum diffusion depth possible during our experiments is about 2 orders of magnitude less than the polymer thickness (r) for the five systems listed. The adsorbates cannot diffuse through the entire polymer depth during the IGC experiments. Any diffusion into the polymer occurring during the experiments must be nonequilibrium diffusion.

If nonequilibrium diffusion is responsible for peak broadening, the retention times decrease with increasing flow rate.[18] As reported by others, we observed that the retention volumes below T_g are independent of flow velocity (see Figure 3).[18,27,30] Nonequilibrium diffusion cannot be responsible for the peak broadening. These data (Figure 3 and Table I) demonstrate diffusion into the polymer is not occurring during IGC below T_g.

Figure 4 shows that the peaks for benzene on PMMA

Table I. Comparison of Average Diffusion Distance, $\langle x \rangle$, with Polymer Thickness, r, for Hydrocarbons in PS, PMMA, and Illinois No. 6 Coal Assuming That the Diffusion Time Is Equal to the IGC Retention Time

polymer	adsorbate	IGC retention time (min)[a,b]	diffusion coeff (cm^2/s)[c]	$\langle x \rangle$ (μm)[d]	r (μm)
PS	n-butane	0.59 (33 °C, 6.9 mL/min)	1.6×10^{-12} (30 °C)[e]	0.84	500
PS	n-pentane	0.75 (33 °C, 7.2 mL/min)	6.3×10^{-13} (30 °C)[e]	0.60	500
PMMA	n-pentane	0.40 (45 °C, 16.2 mL/min)	3.2×10^{-16} (30 °C)[e]	0.01	200
PMMA	n-hexane	1.20 (40 °C, 20.8 mL/min)	5.0×10^{-17} (30 °C)[e]	0.01	200
Illinois No. 6 coal	methane	3.60 (30 °C, 3.1 mL/min)	$\sim 10^{-12}$ (30 °C)[f]	1.70	230

[a] Determined from the first moments of the IGC peaks. [b] Numbers in parentheses are temperatures and flow rates at which measurements were made. [c] Numbers in parentheses are temperatures of diffusion experiments. [d] Calculated using the equation $\langle x \rangle = 2\,(Dt/\pi)^{1/2}$ assuming a diffusion time, t, equal to the IGC retention time. [e] Diffusion coefficients from ref 43. [f] Diffusion coefficients from ref 44.

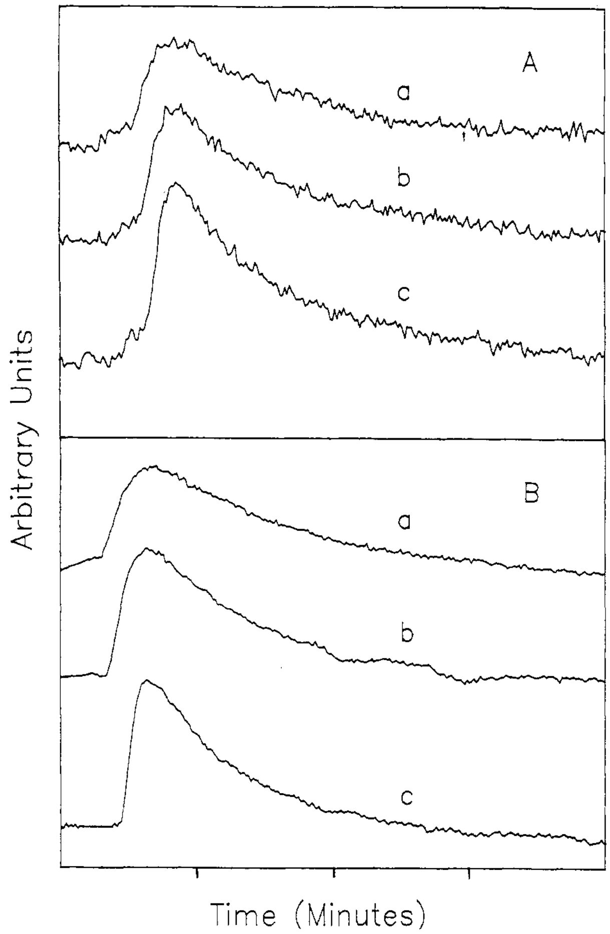

Figure 4. IGC peaks for benzene on poly(methyl methacrylate) and for *n*-pentane on Illinois No. 6 coal. To make clear changes in peak width, the curves have been shifted along the time axis to bring their peak maxima into coincidence. Ticks on the *x*-axis indicate 1-min intervals. Peak widths were measured at 0.607 times the height. (A) Benzene on PMMA, column temperature = 52 °C, injections = 0.015 mL at 0.010 Torr: (a) flow rate = 23.2 mL/min, width = 0.78 min, retention time = 1.70 min; (b) flow rate = 27.9 mL/min, width = 0.66 min, retention time = 1.49 min; (c) flow rate = 34.1 mL/min, width = 0.60 min, retention time = 1.29 min. (B) *n*-Pentane on Illinois No. 6 coal, column temperature = 110 °C, injections = 0.015 mL at 0.013 Torr: (a) flow rate = 28.4 mL/min, width = 0.80 min, retention time = 1.10 min; (b) flow rate = 35.1 mL/min, width = 0.68 min, retention time = 1.00 min; (c) flow rate = 42.7 mL/min, width = 0.53 min, retention time = 0.79 min.

and *n*-pentane on Illinois No. 6 coal decrease with increasing flow rate. The ratio of standard deviation in time units to the retention time, σ_t/t_R, is constant with flow velocity. See Figure 5. Because $\sigma_v = \sigma_t F$, where F is the flow rate, this means that the standard deviation in volume units is constant with flow velocity. The behavior displayed in Figure 5, a constant standard deviation σ_v with flow rate, was observed for every system we studied, including *n*-alkanes on PS and PMMA, tetrahydrofuran and dimethyl sulfoxide on PMMA, and *n*-alkanes and a wide range of polar molecules on Illinois No. 6 coal. We never observed any other dependence of peak width on flow velocity. The behavior in Figures 4 and 5 does not follow the flow rate-dependent behaviors associated with equilibrium diffusion and predicted by the van Deemter equation nor the flow rate-dependent behavior observed for nonequilibrium diffusion.[16,41]

The data demonstrate that neither isotherm nonlinearity nor diffusion into the polymer are responsible for peak broadening below T_g. The only other mechanisms which could be responsible for the broad peaks are gas diffusion or surface desorption. Both of these mechanisms give retention volumes that are sensitive to interactions with the polymer surface only. IGC below T_g is sensitive to surface interactions only, and the retention volumes at sufficiently low injection sizes may be used to determine polymer adsorption thermodynamics.

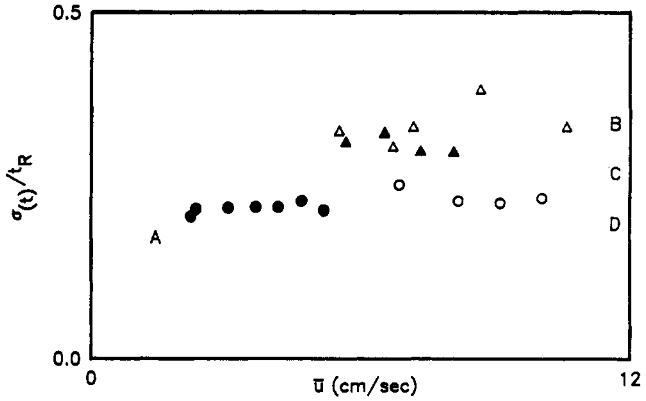

Figure 5. Plots of the ratio of standard deviation in time units to retention time, σ_t/t_R, vs linear flow velocity, $\bar{u}$, for adsorbates on poly(methyl methacrylate) and Illinois No. 6 coal: (A) methane on Illinois No. 6 coal, column temperature = 50 °C, ●; (B) cyclopropane on Illinois No. 6 coal, column temperature = 100 °C, △; (C) benzene on PMMA, column temperature = 52 °C, ▲; (D) neopentane on Illinois No. 6 coal, column temperature = 90 °C, ○.

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