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Adsorption of Aliphatic, Alicyclic, and Aromatic Hydrocarbons on Poly(ethylvinylbenzene-divinylbenzene) Adsorbent at from Effective Zero to Finite Adsorbate Surface Coverage

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The solid/gas partition coefficients, K_s , and related thermodynamic properties of a number of hydrocarbon adsorbates at effective zero surface coverage on commercial samples of the title adsorbent, Porapak Q, were measured over the temperature range 293–443 K. The enthalpies of adsorption derived from the averaged absolute K_s gave incremental ΔH_s° of -7.5 kJ mol^{-1} for aliphatic and alicyclic $-\text{CH}_2-$, as well as aromatic $-\text{CH}=\text{}$, and -12 kJ mol^{-1} for $-\text{CH}_3$, while the differential entropies calculated in terms of translational motions were found to predict correctly the trends observed in the experimental ΔS_s° . The technique of elution by characteristic point (ECP) was then used to derive the finite concentration adsorption isotherms and isosteric heats of adsorption of *n*-hexane, *n*-heptane, cyclohexane, benzene, carbon tetrachloride, and acetone at fractional adsorbate pressures, p/p° , of no greater than 10^{-2} on a particular sample of the title adsorbent at 20° intervals over the temperature range 413–493 K. The isotherms of some adsorbates exhibited inflection points, while others gave linear or Langmuir curve shapes; all were noticeably temperature-dependent. The data for all adsorbates were found to fit the Freundlich expression at from zero surface coverage up to the limit of isotherm inflection (that is, over the concentration range of direct interest in analytical separations), the constants from which were shown to correlate with the adsorbate molar refractions. Adsorbate retentions with the title adsorbent could thereby be approximated from purely molecular properties; extrapolation of the isotherm data to infinite dilution yielded adsorbate partition coefficients that were in fact found to agree with those observed experimentally at zero surface coverage.

Prior to the mid-1960s, the types of stationary phases used in analytical gas-solid chromatography (GSC) were limited primarily to inorganic materials such as silicas, aluminas, zeolites, and various types of graphitized carbon. Synthetic organic polymeric adsorbents in the form of porous beads were then introduced by Hollis (1–3). Very many studies of such supports were published in the few years soon thereafter, roughly half of which dealt with the separation of inorganic adsorbates (e.g., permanent gases) or mixtures of these with organic adsorbates (4). This trend has continued and, at present, there is a considerable literature on the use of synthetic polymers for the GSC analysis of gases as well as trace organic compounds in aqueous matrices. In addition, the adsorbents have since found use as stationary phases in liquid chromatography (5, 6) and as trapping agents for trace-level organic compounds present both in liquid (7) and in gaseous

(8, 9) samples. However, and despite their widely documented advantages, the materials exhibit a number of drawbacks, these including poor batch-to-batch reproducibility (10) and changes in adsorptive properties with time (aging). As a result, they are not as widely used as might otherwise be the case, e.g., in routine quality control carried out with automated data acquisition systems, since retentions cannot be assumed constant from one operating period to the next.

Porapak Q, a copolymer of ethylvinylbenzene and divinylbenzene, is one such synthetic adsorbent that has received considerable attention as a GSC stationary phase. As a result, retentions for very many compounds with this packing have been published, these being collated occasionally in literature issued by the major vendor, Waters Associates, and by others. However, and despite its popularity, there is a paucity of information concerning the thermodynamics of adsorption with this material, hence, only a poor understanding of the factors that govern adsorbate retentions with it. Of those studies that have been carried out, Zado and Fabecic (4) determined, e.g., the heats of adsorption of various organic compounds at zero surface coverage and, since *n*-pentane was observed to exhibit a more negative molar enthalpy of adsorption than water or methanol, Porapak Q was said in that work to be a nonpolar, chemically homogeneous, and notably nonspecific adsorbent. In accordance with this, it was found that the heats of adsorption of the adsorbates were related linearly to the respective polarizabilities (4). Heats of adsorption of some gaseous hydrocarbons and CO_2 on various Porapaks over the temperature interval 303–343 K have also been reported by Castello and d'Amatto (11). In addition, these workers noted that, along with adsorption, adsorbate surface solution appeared as well to contribute to retentions (4, 11). (Thus, "sorption" might well be taken to be more appropriate than "adsorption" in describing adsorbate interactions with these packings; see later.) Retentions and heats of adsorption of halogen-substituted hydrocarbons, C_1 – C_5 hydrocarbons (12), permanent gases, and C_4 hydrocarbons (13) at finite surface coverage and over restricted temperature ranges on Porapak Q have also been described and discussed. However, broadly speaking, such measurements have heretofore been regarded merely as supplemental to those carried out at zero adsorbate surface coverage, since the latter is by far the dominant mode of operation in analytical gas-solid chromatography. Even so, it is not infrequently the case that analytical GSC *must* be carried out beyond the Henry's law region, due if nothing else to the limited sensitivity of some methods of detection.

Accordingly, and in order to study what in principle should be a continuum of adsorbate behavior extending from the limit of infinite dilution to saturated surface concentration, as well as gain in general a broader fundamental understanding of

the mechanism(s) of retentions with Porapak Q as well as related adsorbents, we report here the measurement and systematic interpretation of the thermodynamic properties of adsorption of representative hydrocarbons at zero adsorbate surface coverage over the temperature range 293–493 K and, in addition, their adsorption isotherms and isosteric heats of adsorption at finite surface concentration with this synthetic organic adsorbent. In doing so, we relate also the results obtained with various particle sizes, as well as with different batches comprised of the same particle size, in order to assess what has heretofore been claimed to be poor batch-to-batch reproducibility of the material as well as gauge the role of surface area in the adsorption process.

THEORY

Broadly speaking, the many different static techniques that have been developed for determination of the quantity of gas adsorbed onto a solid surface can be divided on the one hand into volumetric methods, where the amount of vapor removed from the gas phase is measured, and gravimetric methods, in which the increase in mass of the adsorbent is monitored during the course of the absorption process (14). Alternative to these, gas-solid chromatography (GSC) represents a dynamic technique (15, 16) with which the equilibrium distribution of an adsorbate between the vapor phase and the surface of an adsorbent can be determined, provided that there is negligible interference with the adsorption process by the carrier gas. The GSC technique offers in addition a number of well-documented advantages over its static counterparts, particularly in the study of surface interactions at effective zero adsorbate coverage. Thus, interfacial phenomena can be assessed quickly and accurately simply on the basis of retention times and bandwidths and shapes read directly from strip-chart tracings, as can the pertinent equilibrium thermodynamic quantities.

Cremer, Huber, Huber, and Keulemans (17–20), following upon the pioneering studies of frontal analysis (FA) by Glueckauf (21) (LC) and James and Phillips (22) and Gregg and Stock (23) (GC), appear to be the first to utilize gas chromatography for the determination of finite concentration adsorption isotherms from retention times and peak shapes via the technique known commonly today as elution by characteristic point. Several modifications of the original method have since been developed and discussed by many, the GC studies by Kiselev and Yashin (24), Conder (25–27) and Purnell (28–30), and Gray, Guillet, and co-workers (31–33) being particularly noteworthy [as is, in addition, the LC work by Köster and Findenegg (34)].

Briefly, it is possible to show from mass balance considerations (35) that in the limit of negligible column pressure drop and in the absence of flow rate variation as the adsorbate band proceeds through the system, the peak maximum fully corrected net retention volume, V_N/cm^3 , is related to the amount of adsorbed material, $q/\text{mol g}^{-1}$, the quotient $p/RT = c/\text{mol cm}^{-3}$ (inclusive of the adsorbate partial pressure in the gas-phase p at temperature T), and the weight of column adsorbent, $w_S/g = A_S/S$, via the relation

$$V_N = w_S(dq/dc) \quad (1)$$

where R is the gas constant, c is the concentration of adsorbate in the gas phase, A_S/m^2 is the surface area of adsorbent in the column, and $S/\text{m}^2 \text{ g}^{-1}$ is the specific surface area of the adsorbent. Following substitution of the ideal gas law for c , eq 1 is solved for dq and then integrated

$$q = \frac{1}{w_S RT} \int_0^p V_N dp \quad (2)$$

Equation 2 thus relates q to p via V_N , where $q = f(p)$ is one form of the adsorption isotherm.

In practice, the amount of adsorbate sorbed per gram of adsorbent, q , is calculated from the relation (e.g., ref 24)

$$q = n_A S_A / w_S S_t \quad (3)$$

where n_A is the number of moles of adsorbate injected, S_A is the area of the chromatographic trace that is bounded by a vertical line drawn from the time of emergence of a nonretained compound to the adsorbate peak maximum height and which encompasses the entire area of the adsorbate peak, and S_t is the chart area bounded only by the adsorbate peak. The partial pressure of the adsorbate in the gas phase is then found from the expression

$$p = n_A shRT / S_t F_c \quad (4)$$

where $F_c/\text{cm}^3 \text{ min}^{-1}$ is the fully corrected mobile-phase flow rate, $s/\text{cm min}^{-1}$ is the chart speed, and h/cm is the pen displacement at the peak maximum. The uptake of adsorbate (q) may thereby be calculated as a function of p without the need for calibration of the detector, provided that the adsorbate density and molecular weight as well as the volume injected are known accurately (from which n_A can then be calculated) and that the chart speed and flow rate remain constant.

Conder (27) has commented at length on the approximations implicit in the above expressions and, also, has defined and discussed the several factors that must be taken into account if finite concentration sorption isotherms measured by gas chromatography are to correspond to those determined with static apparatus. The largest errors are incurred when the sorption effect and the carrier compressibility are not taken into account. (The sorption effect arises because of changes in the localized mobile-phase velocity as the adsorbate band moves through the column, the net result being a skewing of the peak profile toward the column outlet.) Each of these factors can be minimized, however, by appropriate experimental design and data reduction (16) and by keeping the adsorbate partial pressure, p , well below that of the bulk, p° . Moreover, the nonlinearity of isotherms in GSC (as here), generally speaking, far outweighs any contributions to band broadening occasioned by chromatographic nonideality. There exist in any event several criteria with which the veracity of the derived isotherms can be assessed, which we apply in turn in what follows below.

EXPERIMENTAL SECTION

Materials. Samples of Porapak Q were obtained from various commercial sources; all were vended originally by Waters Associates, Milford, MA. Each was resieved by us to yield packings of 50/80 (297–177 μm), 80/100 (177–149 μm), 100/120 (149–125 μm), 120/140 (125–105 μm), and 170/200 (88–74 μm) U.S. Standard screen. A separate sample of 80/100 mesh Porapak Q was also evaluated, which was purchased from Alltech Associates and which was labeled as batch 1986. The specific surface areas of the solids were determined with a Strohlein areameter using the single-point nitrogen adsorption method. Prior to packing into stainless-steel GC columns, the materials were conditioned overnight in a vacuum oven at 390 K and 2×10^3 Pa.

Permanent gas adsorbates were purchased from Matheson, while the remaining were obtained from various commercial sources; all were of the highest available purity. Six adsorbates, *n*-heptane, cyclohexane, benzene, carbon tetrachloride, and acetone, were selected as representative of several functionalities for the finite concentration measurements. Density data used to calculate n_A were obtained from the compilations by Dreisbach (36) and Riddick and Bunger (37). Helium was the carrier in the experiments involving the laboratory-constructed gas chromatograph, while nitrogen was employed with the modified analytical gas chromatograph (see below).

Apparatus. Two gas chromatographs were employed in the course of these studies. The laboratory-constructed high-precision apparatus (thermal conductivity detection) has been detailed elsewhere (38) and its precision, accuracy, and potential sources

of error discussed at length (39). This apparatus was used over the temperature span 293–443 K.

A Perkin-Elmer Model 881 analytical gas chromatograph, adapted for physicochemical measurements, was used at temperatures of from 413 to 493 K. The original instrument was replumbed to a single-column system, and provision was made for measuring the carrier gas inlet pressure with a mercury manometer. The temperature of the forced-air column thermostat was measured with a mercury thermometer sited in one or another various holes drilled through the oven wall. The detector was an FID.

To assess the precision and accuracy of the modified analytical instrument, the liquid–gas partition coefficients, K_R , of several hydrocarbon solutes (*n*-hexane, *n*-heptane, benzene, cyclohexane, chloroform, and dichloromethane) were measured with squalane solvent. The values observed agreed with literature data known to be of high accuracy (39–44) to within experimental error when the solute–carrier virial effects with nitrogen (45, 46) were taken into account. Interlaboratory comparison of experimental K_S for a given temperature and common adsorbent (e.g., 80/100-mesh Porapak Q, batch 1986) was also carried out with the two apparatus; the results agreed to within at worst $\pm 5\%$, depending on the adsorbate. In order to gauge in addition whether the partition coefficients corresponded in fact to equilibrium, the K_S of several representative adsorbates (*n*-hexane, benzene, and cyclohexane) were determined with the laboratory-constructed apparatus at flow rates ranging from 20 to 104 cm³ min⁻¹. The results established that the partition coefficients were indeed independent of the carrier velocity to within ca. $\pm 2\%$. The partition coefficient data derived from either instrument thus fell overall well within the limits of experimental error of the specific surface area measurements and, more importantly, within the batch-to-batch variation of the properties of a given mesh size of adsorbent (see later).

Procedures. For the studies of zero surface coverage, the smallest detectable amounts of gases or vapors were injected with a Hamilton 10- μ L syringe. Each adsorbate was run at least 3 times; the raw retentions, t_R , were measured with a stopwatch and cross-checked against tracings obtained with a strip-chart recorder. All peaks exhibited acceptable symmetry, and the retentions were independent of the amount of (highly dilute) vapor introduced onto the columns. Adsorbate net retention volumes, V_N , were then calculated from the expression

$$V_N = j(t_R - t_A)F_c \quad (5)$$

where j is the James–Martin gas compressibility correction factor, F_c is the carrier corrected flow rate, and t_A is the retention time of an unretained compound. For the laboratory-constructed apparatus, with which lower temperatures were employed, the retention time of argon was taken as that corresponding to nonsorbed species. That of methane was used for the determination of t_A in the experiments involving the modified analytical GC at higher temperatures. The carrier corrected flow rate, F_c , was calculated from the raw flow rate, F_{fm} , the latter measured with a soap bubble flowmeter at temperature T_{fm} , under the assumption that the ratio of carrier virial effects at the column and flowmeter temperatures approximately cancel, i.e.

$$F_c = F_{fm} \left(\frac{T_c}{T_{fm}} \right) \left(\frac{p_0 - p_w}{p_0} \right) \quad (6)$$

where T_c is the column temperature, p_0 is the column outlet pressure (taken as barometric), and p_w is the vapor pressure of water at T_{fm} . The surface partition coefficient, K_S , defined here as the net retention volume per unit surface area of adsorbent A_S , was then calculated as

$$K_S = V_N/A_S \quad (7)$$

where A_S is the product of the specific surface area S/m^2 g⁻¹ and the weight of adsorbent in the column, w_S . K_S thus has units of distance. The thermodynamic properties of adsorption were derived from the temperature dependence of the adsorbate K_S as follows. The standard-state free energy of adsorption, ΔG_S° , was calculated first from the relation (47, 48)

$$\Delta G_S^\circ = -RT_c \ln (K_S p_A^\circ / \pi_s) \quad (8)$$

where R is the gas constant, T_c is the column temperature, p_A° is the adsorbate standard-state vapor pressure, and π_s is the two-dimensional standard-state (surface) spreading pressure of the adsorbed gas, and where the reference states were taken (48, 49) as $p_A^\circ = 101 \text{ kN m}^{-2}$ (1 atm) and $\pi_s = 0.338 \text{ mN m}^{-1}$. The differential heats of adsorption of the adsorbates at zero coverage, i.e., the standard-state enthalpies of adsorption, $-\Delta H_S^\circ$, were obtained from the temperature dependence of K_S , viz.

$$d(\ln K_S)/d(1/T) = -\Delta H_S^\circ/R \quad (9)$$

The corresponding standard-state entropies of adsorption, ΔS_S° , were then calculated from

$$\Delta S_S^\circ = (\Delta H_S^\circ - \Delta G_S^\circ)/T \quad (10)$$

For the studies at finite surface coverage, isotherms were constructed from 15–20 individual injections of each adsorbate (comprising liquid sample volumes of from 0.1 to 25 μ L) onto 80/100-mesh Porapak Q, batch 1986. These amounts resulted in isotherms covering fractional adsorbate pressures, p/p° , of up to ca. 10^{-2} . Data reduction was then carried out as described in the theory section and as discussed in what follows.

RESULTS AND DISCUSSION

Adsorbate Retentions at Zero Surface Coverage. A representative portion of the results for the adsorbate partition coefficients (413 K) is provided in Table I, the data being indicative of the trends observed throughout this work. Also shown are the specific surface areas of the adsorbents.

Batchwise Variations of the Adsorbent. We found, first, that there was no direct connection between mesh size and surface area for the samples we had to hand whereas, with uniform density and specific pore volume (cm³ g⁻¹), the specific surface area, S , must otherwise increase with decreasing particle size. In addition, the adsorbate absolute K_S were observed in this work to fluctuate irregularly with the adsorbent surface area, where the partition coefficients of individual compounds differed by as much as 60–70% from one mesh size to another. For example, that for methylcyclohexane with 170/200-mesh Porapak ($S = 536 \text{ m}^2 \text{ g}^{-1}$) was $0.562 \text{ cm}^3 \text{ m}^{-2}$, while with 80/100-mesh material ($S = 504 \text{ m}^2 \text{ g}^{-1}$) the value increased to $0.932 \text{ cm}^3 \text{ m}^{-2}$. Further, the variations cannot be attributed directly to differences in pore volume and/or distribution, since Johnson and Barrell (50) found that the micropore morphology of porous polymers of these types was approximately constant from one to the next (even though their chromatographic properties were very substantially different).

The quite large batch-to-batch disparities in retentions with various Porapaks have also been reported and discussed by others (6, 10). In addition, several have postulated that the effects are due to variations in the manufacturing process, for example, the initial *m*-*p*-divinylbenzene and ethylvinylbenzene ratios used and the type and extent of cross-linking employed (51, 52) (cf. in particular Figure 1 of the latter). These result in turn in variations, inter alia, in the residual surface vinyl content. Accordingly, taking advantage of differences in the batch-to-batch adsorbent selectivity (53) might appear at first glance to be far more beneficial in achieving separations than would be enhancement of the system efficiency, e.g., by effecting a decrease in the packing particle size. However, it was found for all samples of Porapak Q used here that plots of $\ln K_S$ against carbon number for the *n*-alkane adsorbates were linear; moreover, all exhibited slopes that were within ca. $\pm 2\%$ of unity. (This is as expected since, presumably, only nonspecific interactions obtain for *n*-alkane adsorbates.) Also, the retention indexes of all adsorbates were found to be approximately independent of the mesh size of the packings. Thus, while the absolute retentions were observed to vary considerably, the adsorbate relative retentions were found to be invariant with particle size as well as surface

Table I. Partition Coefficients, $K_S/\text{cm}^3 \text{ m}^{-2}$, for Listed Adsorbates at Zero Effective Surface Coverage on Porapak Q Adsorbents of Indicated Mesh Size and Surface Area at 413 K

adsorbate	T_b/K	$K_S/\text{cm}^3 \text{ m}^{-2}$					
		50/80 mesh ($516 \pm 1 \text{ m}^2 \text{ g}^{-1}$)	80/100 mesh ($486 \pm 11 \text{ m}^2 \text{ g}^{-1}$)	80/100 mesh ^a ($504 \pm 23 \text{ m}^2 \text{ g}^{-1}$)	100/120 mesh ($432 \pm 35 \text{ m}^2 \text{ g}^{-1}$)	120/140 mesh ($500 \pm 4 \text{ m}^2 \text{ g}^{-1}$)	170/200 mesh ($536 \pm 4 \text{ m}^2 \text{ g}^{-1}$)
1. <i>n</i> -pentane	309.4	0.097	0.112	0.110	0.130	0.121	0.084
2. <i>n</i> -hexane	342.2	0.240	0.294	0.311	0.342	0.319	0.212
3. <i>n</i> -heptane	371.6	0.595	0.767	0.790	0.903	0.770	0.526
4. <i>n</i> -octane	399.0	1.589			2.298	2.009	2.332
5. cyclohexane	354.6	0.285	0.359	0.378	0.412	0.376	0.266
6. methylcyclohexane	373.5	0.609	0.768	0.932	0.913	0.797	0.562
7. benzene	353.3	0.270	0.309	0.320	0.362	0.335	0.259
8. toluene	383.8	0.761	0.848	0.887	0.979	0.942	0.680
9. dichloromethane	313.3	0.069	0.076	0.084	0.090	0.086	0.060
10. chloroform	334.5	0.165	0.183	0.211	0.211	0.210	0.156
11. tetrahydrofuran	337.2	0.185	0.189	0.208	0.223	0.222	0.183
12. thiophene	357.3		0.281		0.344	0.441	0.250

^a Batch 1986. ^b Modified analytical GC; remaining data obtained with high-precision apparatus.**Table II. Heats of Adsorption, ΔH_S° , and Liquefaction, ΔH_L° , and Molar Refractions, R_m° , and Averaged^b Free Energies of Adsorption, ΔG_S° for Indicated Adsorbates with Porapak Q Adsorbent at 443 K**

adsorbate	$-\Delta H_S^\circ/\text{kJ mol}^{-1}$			$-\Delta H_L^\circ/\text{kJ mol}^{-1}$	$R_m/\text{cm}^3 \text{ mol}^{-1}$ ^a	$-\Delta G_S^\circ/\text{kJ mol}^{-1}$ ^b
	exptl	lit.	calcd			
ethane	24.2 ± 0.8^c	23.9^d	24.0	9.67		
propane	32.5 ± 0.8^c	36.24^e	31.5	15.1	16.05	
ethylene	22.3 ± 0.8^c					
propylene	32.5 ± 0.8^c					
<i>n</i> -pentane	45.3 ± 2.8	47.30^e	46.5	28.3	25.27	10.17
<i>n</i> -hexane	52.5 ± 3.7	57.5^f	54.0	31.5	29.91	13.12
<i>n</i> -heptane	59.8 ± 1.8		61.5	36.6	34.55	16.06
<i>n</i> -octane	67.6 ± 5.0		69.0	41.5	39.19	19.06
cyclohexane	50.7 ± 3.7	54.42^e	45.0	33.0	27.71	13.98
methylcyclohexane	56.1 ± 2.5		57.0	35.4	32.50	16.34
benzene	48.3 ± 2.5	54.00^e	45.0	33.8	26.18	13.59
		51.5^f				
toluene	56.5 ± 2.7	60.3^f	57.0	38.0	31.10	16.71
dichloromethane	43.1 ± 3.0			28.6	16.36	9.04
chloroform	42.6 ± 3.8			30.8	21.46	11.91
carbon tetrachloride	44.8 ± 2.7^c			33.1	26.44	
tetrahydrofuran	49.1 ± 2.7					12.12
thiophene	50.2 ± 0.9				24.37	13.27
acetone	36.2 ± 5.5^c	40.6^e				

^a Reference 36. ^b Average of results with mesh sizes 80/100, 100/120, and 120/140 at 443 K. ^c Batch 1986 Porapak Q; $T_c = 293\text{--}348 \text{ K}$.^d Reference 13. ^e Reference 4. ^f Calculated from data reported in ref 8.

area and, hence, will in all likelihood prove to be the most useful measures with which to characterize straightforward analytical applications. Nevertheless, there is merit in considering the absolute retentions in greater detail since, in any event, ratios of these govern what separations can be achieved in practice.

Thermodynamic Properties of Adsorption with Porapak Q. The enthalpies of adsorption of the adsorbates, calculated from the least-squares slopes of plots of eq 9, are presented in Table II. The data for each adsorbate comprise the ΔH_S° averaged over all mesh sizes and are shown together with the corresponding standard deviations.

Comparison, first, of the enthalpies of this work with those reported in the literature, column 3 of Table II, indicates a level of agreement that corresponds to the experimental error of the GSC method, which in turn implies that ΔH_S° can be expected to be approximately independent of the batch of the adsorbent. That is, while plots of $\ln K_S$ against T^{-1} may exhibit different intercepts, the slopes (hence, the batchwise temperature dependence of separations) appear to be nearly invariant.

Also, we found that the ΔH_S° values for *n*-hexane, cyclohexane, and benzene were roughly identical, the average for these three adsorbates being $-50.0 \pm 2.1 \text{ kJ mol}^{-1}$. The same was observed as well for *n*-heptane, methylcyclohexane, and toluene, i.e., chemically different compounds with the same number of carbon atoms, which implies that the interactions between the adsorbates and Porapak Q are nonspecific. Accordingly, we plotted ΔH_S° against carbon number of the *n*-alkanes and calculated from the slope and the data of Table II an incremental enthalpy, ΔH_S° ($-\text{CH}_2-$, $-\text{CH}=\text{}$), for aliphatic and alicyclic methylene as well as aromatic methine of -7.5 kJ mol^{-1} . Also, we found an incremental enthalpy of adsorption for methyl, ΔH_S° ($-\text{CH}_3$), of -12 kJ mol^{-1} . The ΔH_S° predicted with these values are then presented in column 4 of Table II. These could of course be refined further by distinguishing between, say, aliphatic and alicyclic methylene units (54, 55); however, doing so does not appear to us to be warranted at the present time given at the very least the batchwise disparities of the absolute K_S . Thus, we regard the incremental ΔH_S° as approximate, which should nevertheless prove useful in predicting (to the same degree of approxi-

Table III. Calculated Translational and Experimental Entropies for Indicated Adsorbates with Porapak Q Adsorbent at 443 K

adsorbate	$^3S_t/J$ $\text{mol}^{-1} \text{K}^{-1}$	$^2S_t/J$ $\text{mol}^{-1} \text{K}^{-1}$	$-\Delta S_t/J$ $\text{mol}^{-1} \text{K}^{-1}$	$-\Delta S_s^\circ/J$ $\text{mol}^{-1} \text{K}^{-1}$
ethane	159.5	110.3	49.2	
propane	164.2	113.5	50.7	
ethylene	158.6	109.7	48.9	
propylene	163.7	113.1	58.1	
<i>n</i> -pentane	171.2	118.2	53.0	79.3
<i>n</i> -hexane	172.6	119.1	53.5	88.9
<i>n</i> -heptane	174.5	120.3	54.2	98.7
<i>n</i> -octane	176.1	121.4	54.7	110.0
cyclohexane	172.3	118.9	53.4	82.9
methylcyclohexane	174.2	120.2	54.0	89.8
benzene	171.4	118.3	53.1	78.4
toluene	173.4	119.6	53.8	89.8
dichloromethane	172.4	119.0	53.4	76.9
chloroform	176.7	121.8	54.9	69.3
carbon tetrachloride	179.8	123.9	55.9	
tetrahydrofuran	170.4	117.6	52.8	83.5
thiophene	172.3	118.9	53.4	83.4
acetone	167.7	115.8	51.9	

mation) variation of the surface partition coefficients (hence, separations) as a function of the column temperature.

The absolute entropies of adsorption of the adsorbates were calculated next according to the method of de Boer (56) and as detailed by us elsewhere (48). The three-dimensional translational entropy of the adsorbate as an ideal gas is given by

$$^3S_t = R \ln (M^{3/2} T^{5/2}) - 9.62 \quad (11)$$

where M is the molar mass of the adsorbate, and where the entropy, 3S_t , is expressed in $\text{J mol}^{-1} \text{K}^{-1}$. Similarly, considering the adsorbate to be an ideal gas having unrestricted freedom of movement in two directions and no freedom of movement in a direction perpendicular to the surface of the adsorbent, the two-dimensional translational entropy is calculated from

$$^2S_t = R \ln (MTA) + 275.32 \quad (12)$$

where A is the area of the adsorbent available for adsorption of an adsorbate molecule in its standard state; taking that defined by de Boer (56), A is $4.08T \times 10^{-6} \text{ cm}^2$.

The calculated 3S_t and 2S_t , together with the predicted $-\Delta S_t$ and the experimental $-\Delta S_s^\circ$ (eq 10; ΔH_s° , averaged ΔG_s° of Table II), are given in Table III. The experimental values are uniformly larger than those forecast from simple translational considerations, which is undoubtedly due to the additional constraints of restricted rotational and vibrational freedom imposed on the adsorbates as a result of being adsorbed on a surface. For example, one translational degree of freedom is lost in favor of a vibrational mode normal to the plane of the surface, while free rotation in the gas phase is reduced to hindered rotation in the adsorbed state. Even so, the calculated $-\Delta S_t$ values correctly predict at least the trends observed in $-\Delta S_s^\circ$ for the aliphatic, alicyclic, and aromatic hydrocarbons. Thus, both sets of data show an increase in magnitude (decreased entropy) on passing from *n*-pentane through *n*-octane, while the values for the cyclic compounds are notably less (increased entropy) than those for the aliphatic solutes of the same carbon number.

Liquidlike Behavior of Porapak Q. It is commonly observed in gas-liquid chromatography (GLC) that cycloalkanes are retained more strongly than *n*-alkanes of corresponding carbon number, while the reverse of this obtains generally with inorganic adsorbents in GSC. The K_s for *n*-hexane, *n*-heptane, cyclohexane, and methylcyclohexane (Table I) conform to the former trend, from which it might be inferred that adsorbate interactions with Porapak Q are more liquidlike than has

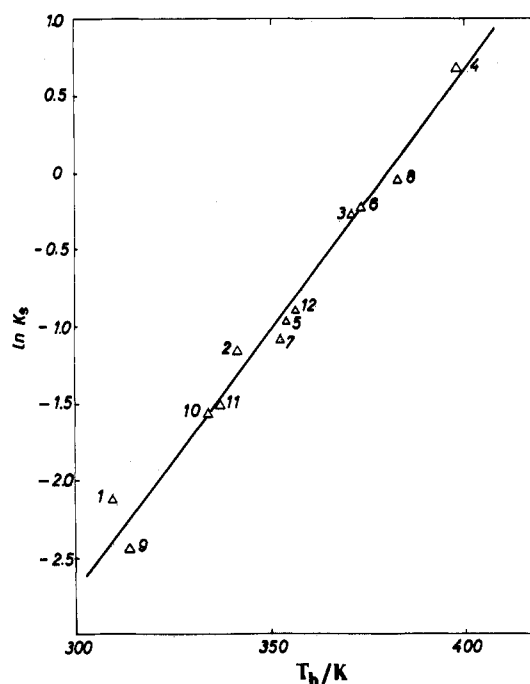


Figure 1. Regression of $\ln K_s$ against boiling point, T_b , for indicated adsorbates (numbering corresponds to sequence given in Table I) with 120/140-mesh Porapak Q.

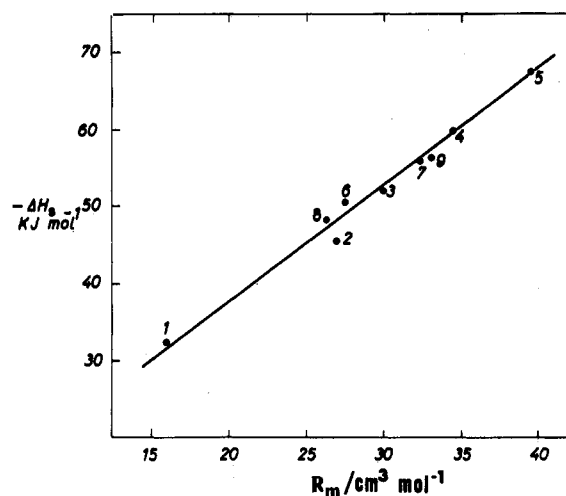


Figure 2. Regression of ΔH_s against molar refraction, R_m , for the following solutes: (1) propane, (2) *n*-pentane, (3) *n*-hexane, (4) *n*-heptane, (5) *n*-octane, (6) cyclohexane, (7) methylcyclohexane, (8) benzene, and (9) toluene.

heretofore been supposed. Indeed, the retentions of all compounds studied here were found to increase with increasing compound boiling point (T_b), as illustrated in Figure 1 ($\ln K_s$ regressed against T_b). However, comparison of the heats of adsorption with those of liquefaction (36), columns 2 and 5 of Table II, shows that the former are everywhere considerably larger than the latter within the temperature range over which this work was carried out. Moreover, there is no immediately apparent correlation between the two sets of data, nor would one be expected, since the magnitudes of the heats of liquefaction depend only on interactions in the bulk, while for the heats of adsorption the energy released corresponds to interactions of the adsorbates with the surface of the adsorbent. Also, we found a good correlation of ΔH_s° with the adsorbate molar refraction, R_m (hence, the electronic component of the polarizability, α), as shown in Figure 2. There is therefore some weight lent the view that the retentions of the adsorbates are due virtually entirely to adsorption, and that what liquidlike solvation there might be of the adsorbent surface

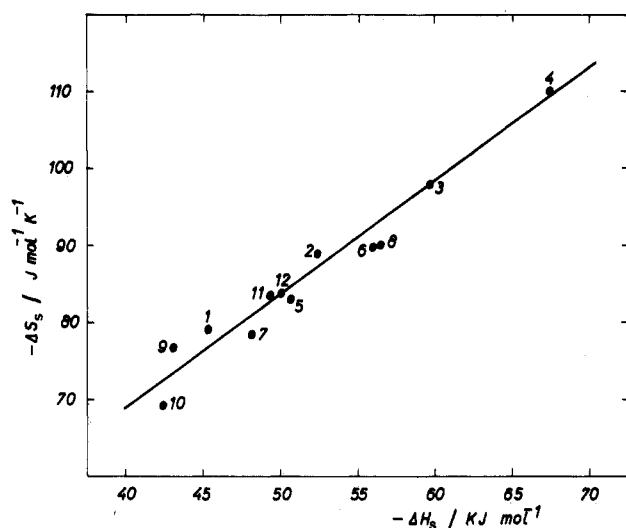


Figure 3. "Compensation" plot for the adsorbates listed in Table I at 443 K.

appears in fact to be negligible. Nevertheless, we do not discount the possibility of the thermal "softening" of the adsorbent at elevated temperatures, as suggested by Gearhart and Burke (57). We are currently exploring this property of Porapak Q and intend reporting soon on the effects that the phenomenon may have on retentions.

Nonspecific Selectivity of Porapak Q. The linear correlations shown in Figures 1 and 2 reinforce the notion that the adsorbate-adsorbent interactions are remarkably nonspecific. Further supportive evidence of this is provided by comparison of the partition coefficients of the aromatic hydrocarbons (benzene and toluene) with those of the *n*-alkanes (*n*-hexane, *n*-heptane) and cycloalkanes (cyclohexane, methylcyclohexane) of the same carbon numbers. The results show that there are in fact no significant π -bond interactions with Porapak Q. Moreover, so-called "compensation" plots of ΔH_s° against ΔS_s° , an example of which is shown in Figure 3 for the partition coefficient data at 443 K, were found to be comprised at each temperature of a single straight line for all adsorbates employed here, viz., representative aliphatic, alicyclic, aromatic, chloroaliphatic, and heterocyclic compounds. We are therefore led to conclude that no specific interactions are apparent for the adsorbates to hand; that is, the adsorbent behaves simply as a cross-linked hydrocarbon. In the nomenclature of Kiselev and Yashin (58), the adsorbates thus fall into groups A and B, and the adsorbent is type I.

Adsorbate Retentions at Finite Surface Coverage. Figure 4 presents an example of the chromatograms (473 K) obtained from the injection of various amounts of carbon tetrachloride onto 80/100-mesh Porapak Q (batch 1986 was used throughout this portion of the work). The band shapes are representative of the magnitude of peak distortion that we observed throughout the finite concentration studies.

Boundary Profiles. We found, first, that there was an excellent coincidence in all cases of the diffuse edges of those peaks corresponding to the six or seven largest amounts injected (cf. Figure 4). In addition, the sharp boundaries of the bands were vertical except in the immediate vicinity of the base line. These results indicate that the predominant factor governing bandwidths was isotherm curvature, rather than the usual kinetic effects that give rise generally to chromatographic nonideality. However, the sharp boundaries of peaks corresponding to the smallest amounts injected were broadened substantially. Also, their maxima described curves that, when connected with those corresponding to the larger amounts injected, resulted in points of inflection. Thus, both nonideality and isotherm nonlinearity contributed to the

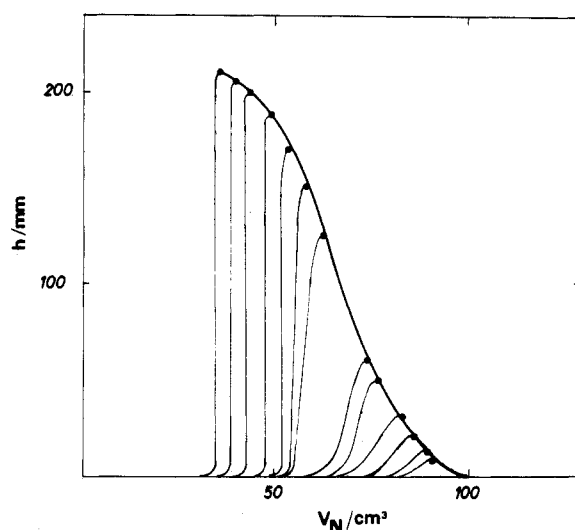


Figure 4. Chromatographic peaks obtained for various amounts of carbon tetrachloride injected onto 80/100-mesh Porapak Q (batch 1986) at 473 K: injection volumes, 0.1, 0.2, 0.3, 0.5, 0.8, 1.0, 3.0, 5.0, 8.0, 12.5, 15.0, 17.5, and 20.0 μ L. Dots indicate peak maxima.

shapes of these peaks, and they were therefore not considered further.

Derivation and Interpretation of Isotherm Data. The areas of the largest peaks whose maxima exhibited smooth coincidence were employed to calculate the isotherms in accordance with eq 1 and 2. Figures 5 and 6 present the results obtained at 20° intervals over the range 413–493 K for the adsorbates *n*-hexane, cyclohexane, benzene, carbon tetrachloride, and acetone; the points shown in Figure 5 were derived with the two different instruments and at various carrier flow rates.

We found, first, that there were no significant discrepancies in the results from one instrument to the other apart from the experimental scatter arising with each, which amounted overall to ca. $\pm 5\%$ as commented upon in the Experimental Section. Moreover, the finite concentration runs carried out with the analytical gas chromatograph were performed after completion of all other measurements, i.e., after several months' use of the columns. The goodness of fit of the data thus belie any effects due to aging of the adsorbent. Also, we observed that the isotherm data were independent of the carrier velocity, which indicates that equilibrium partitioning was in fact extant throughout chromatographic migration of the adsorbate bands. Illustration of this is provided in Figure 7, where the lower part of the cyclohexane isotherm is presented and where the data were obtained at flow rates ranging from 61 to 144 $\text{cm}^3 \text{min}^{-1}$.

Application of the Clausius-Clapeyron equation to the adsorption isotherms next yielded the isosteric (i.e., constant surface coverage) heats of adsorption, q_{st} (59)

$$\left[\frac{\partial(\ln p)}{\partial(1/T)} \right]_q = - \frac{q_{st}}{R} \quad (13)$$

The isosteres found for benzene are shown in Figure 8 and are representative of those observed for the remaining adsorbates. Figure 9 then presents plots of $q_{st}/\text{kJ mol}^{-1}$ against surface coverage $q/\text{mol g}^{-1}$ for *n*-hexane, cyclohexane, benzene, and carbon tetrachloride adsorbates, where the error bars correspond to $\pm 5\%$ of the (ordinal) heats. The upper two of these (*n*-hexane, cyclohexane) illustrate that with increased surface coverage the values of q_{st} approach asymptotically the respective heats of liquefaction, ΔH_L , as might ordinarily be expected. However, the same is not true for the remaining two adsorbates, although whether the deviations shown are real or artifactual is not clear at the present time. For ex-

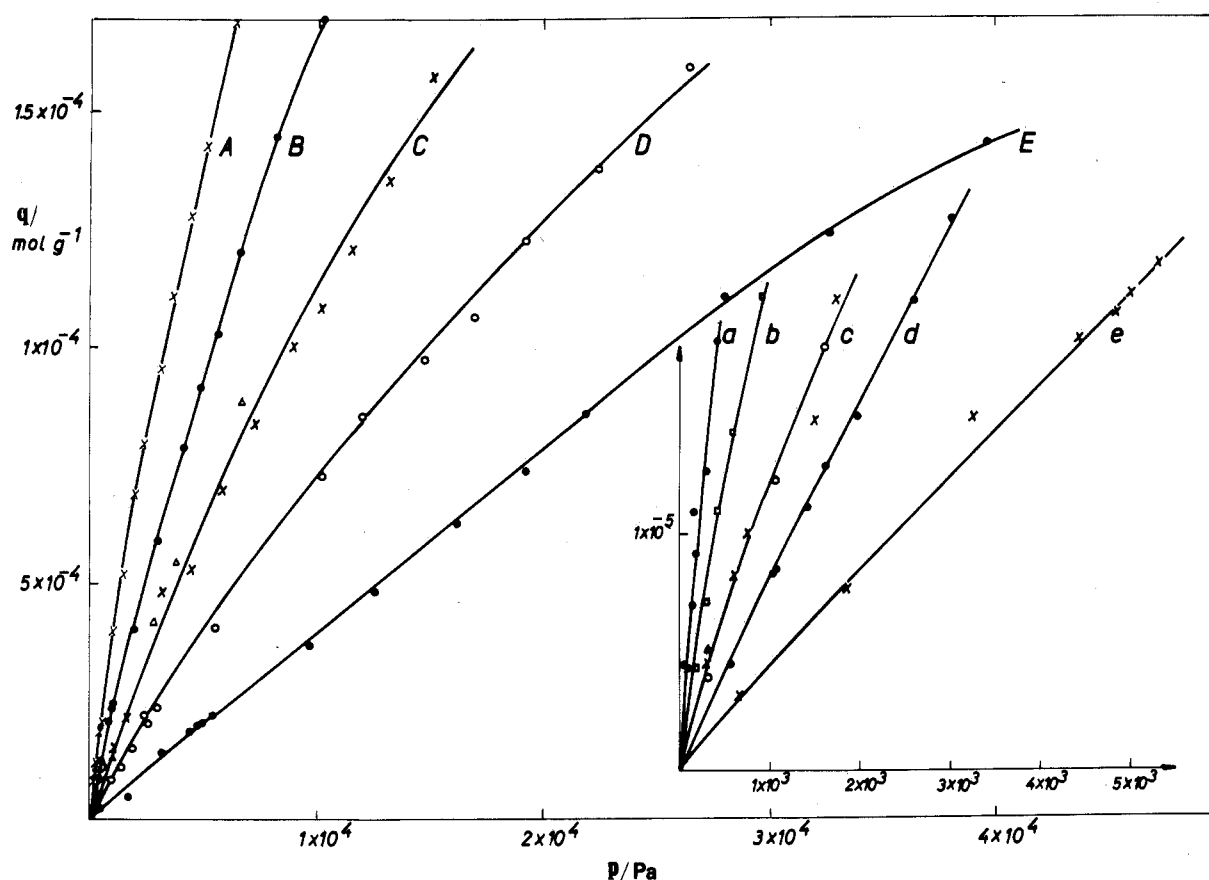


Figure 5. Adsorption isotherms for *n*-hexane on 80/100-mesh Porapak Q (batch 1986) at (A) 413 K, (B) 433 K, (C) 453 K, (D) 473 K, and (E) 493 K. Insert: lower regions of the isotherms at (a) 413 K, (b) 433 K, (c) 453 K (crosses, high-precision GC; open circles, analytical GC), (d) 473 K, and (e), 493 K. Flow rate varied in C as follows: crosses, 27.4 cm³ min⁻¹; squares, 42.6 cm³ min⁻¹; triangles, 18.1 cm³ min⁻¹.

Table IV. Freundlich Constants^a (eq 14) and Molar Refractions^b for Indicated Adsorbates with Porapak Q Adsorbent at 433 K

adsorbate	$-\log k$	$1/n$	$R_m/\text{cm}^3 \text{mol}^{-1}$
<i>n</i> -hexane	2.8522	0.9258	29.91
<i>n</i> -heptane	2.3519	0.9657	34.55
cyclohexane	2.5846	0.9760	27.71
benzene	2.6289	0.9756	26.18
carbon tetrachloride	2.8690	0.8443	26.44
acetone	3.2565	0.9018	16.18

^a Pressure in atmospheres. ^b Reference 36, 293 K.

ample, Katz and Gray (33) have described a number of systems for which q_{st} was observed to exhibit a sharp increase with increasing surface coverage, as well as others where the converse was true. In the present instance, the drifts in q_{st} for three of the four adsorbates (as well as the maximum exhibited by benzene) at far below monolayer coverage suggest that Porapak Q is comprised of a strongly nonuniform surface (including that contained within the micropore structure). (There may well also be substantial differences in the ability

of the solutes to penetrate, then interact with, the microporous structure of the adsorbent.) A heterogeneous distribution of types of sites available for adsorption could result from surface variations in the residual vinyl content, as mentioned previously. In addition, compositional variations of the polymer could conceivably give rise to thermal "softening" that is localized at the microscopic level. This might take the form, for example, of point-to-point variations in glass transition temperatures.

Further interpretation of the isotherm data in terms of the Brunauer-Emmett-Teller (BET) theory (60) of multilayer adsorption was not attempted, since the adsorbate fractional pressures, p/p° , utilized in this work did not exceed 10^{-2} , whereas the range of applicability of the BET formulation is generally regarded as ca. 0.05–0.3. The Freundlich isotherm (61) was therefore employed as an alternative, where fitting of the isotherm data corresponding to near-zero surface coverage (i.e., well below any inflection points) was carried out with the log form expression

$$\log q = \log k + (1/n) \log p \quad (14)$$

where q and p are as defined above and where k and n are

Table V. Comparison of Partition Coefficients, $K_s/\text{cm}^3 \text{m}^{-2}$, Derived from Finite Concentration Data and eq 15 and from Measurements at Zero Surface Coverage (ZSC) for Indicated Adsorbates on Porapak Q Adsorbent

adsorbate	$K_s/\text{cm}^3 \text{m}^{-2}$									
	413 K		433 K		453 K		473 K		493 K	
	eq 15	ZSC	eq 15	ZSC	eq 15	ZSC	eq 15	ZSC	eq 15	ZSC
<i>n</i> -hexane	0.299	0.306	0.181	0.166	0.100	0.104	0.060	0.065	0.033	0.035
cyclohexane	0.352	0.363	0.213	0.218	0.129	0.136	0.064	0.069	0.048	0.049
benzene			0.195	0.201	0.113	0.116	0.068	0.083	0.045	0.049
carbon tetrachloride			0.188	0.198	0.108	0.112	0.072	0.074	0.041	0.049
acetone			0.061	0.061	0.036	0.040	0.024	0.027	0.018	0.021

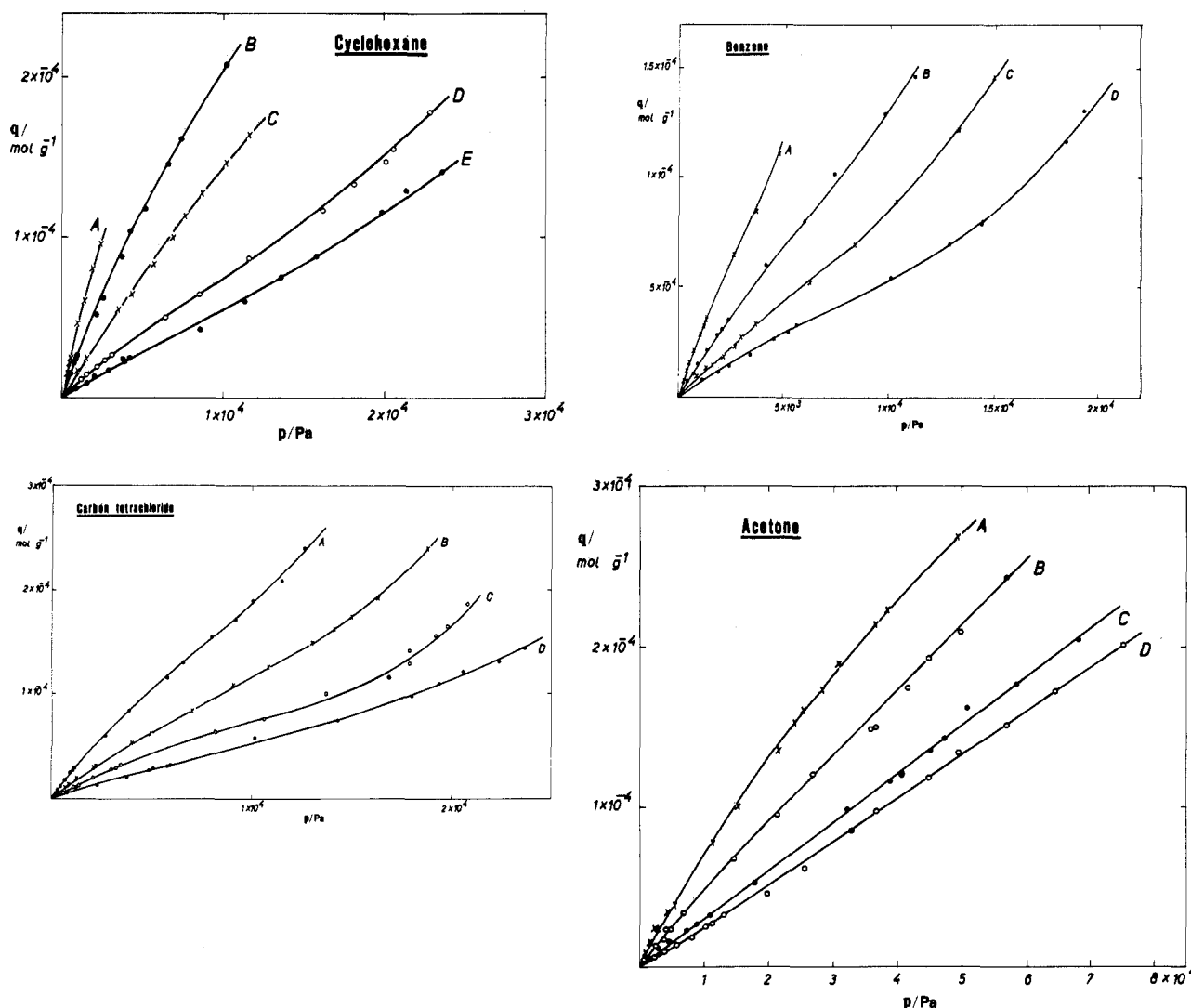


Figure 6. Adsorption isotherms for indicated adsorbates on 80/100-mesh Porapak Q (batch 1986) at (a) 413 K (A), 433 K (B), 453 K (C), 473 K (D), and 493 K (E); and (b-d) 433 K (A), 453 K (B), 473 K (C), and 493 K (D).

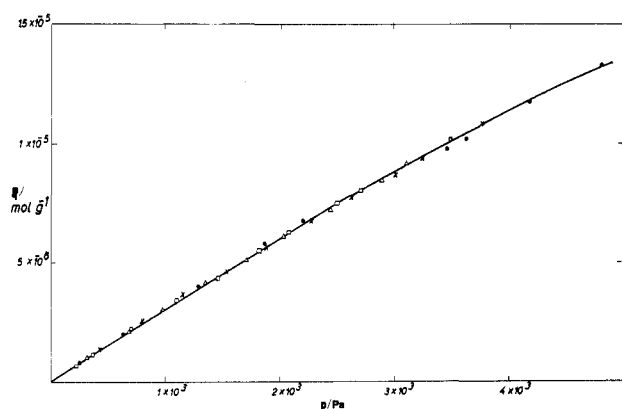


Figure 7. Adsorption isotherm for cyclohexane on 80/100-mesh Porapak Q (batch 1986) at 433 K and at various carrier flow rates: filled circles, 61 cm³ min⁻¹; triangles, 85 cm³ min⁻¹; squares, 114 cm³ min⁻¹; and crosses, 144 cm³ min⁻¹.

temperature-dependent constants whose values vary from one adsorbate to another. Examples of the best-fit k and n at 433 K, obtained with eq 14 (p in atm) by regression analysis for the systems at hand, are presented in Table IV, while comparisons of the resultant calculated isotherms are made with the observed experimental data for n -hexane in Figure 10.

Dubinin (62) among others has shown that the Freundlich constants with a given adsorbent are often related to physi-

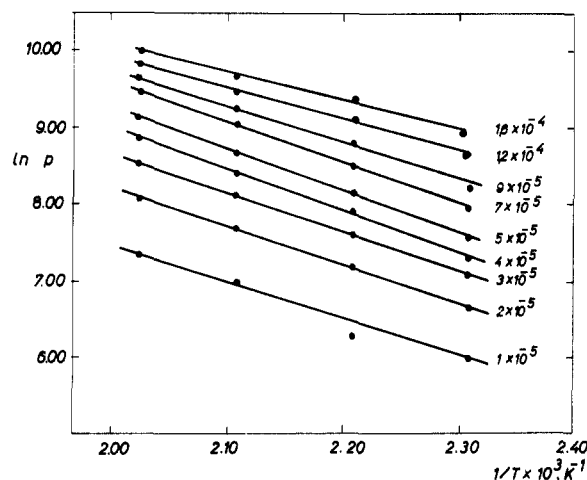


Figure 8. Isotheres for benzene on 80/100-mesh Porapak Q (batch 1986) at indicated constant surface coverages, q /mol g⁻¹.

cochemical properties of the adsorbates, viz., molar volume, molar refraction, and the parachor. Accordingly, we show in Figure 11 the molar refractions (Table IV) of the adsorbates of this work regressed against n^{-1} (upper plot, greatly magnified ordinate scale) and against $\log k$. Similar correlations were found at other temperatures, which we regard as another indication of the nonspecific nature of Porapak Q adsorbent.

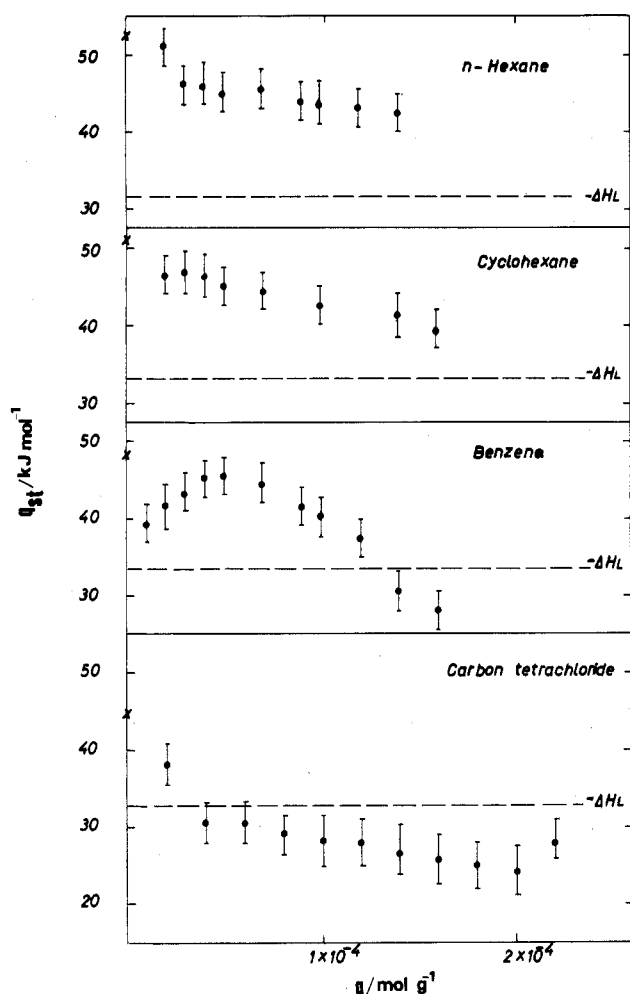


Figure 9. Plots of isosteric heats of adsorption against surface coverage for indicated adsorbates obtained with 80/100-mesh Porapak Q (batch 1986). Error bars correspond to $\pm 5\%$ on q_{st} . Crosses, ΔH_S from measurements at zero surface coverage; horizontal dashed lines, molar heats of liquefaction, ΔH_L .

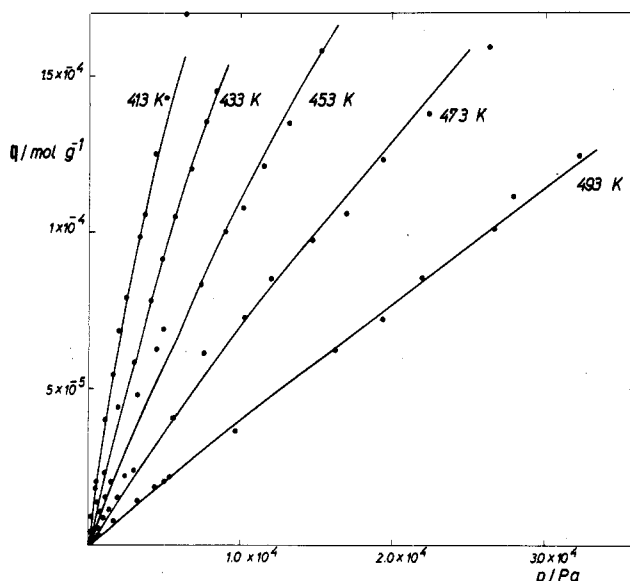


Figure 10. Adsorption isotherms for *n*-hexane on 80/100-mesh Porapak Q (batch 1986) at indicated temperatures: filled circles, experimental results; solid lines, calculated with eq 14 and best-fit Freundlich constants.

Moreover, the results portend that the Freundlich constants can at least be approximated on an a priori basis, from which it follows that the isotherms (thence, ultimately, analytical

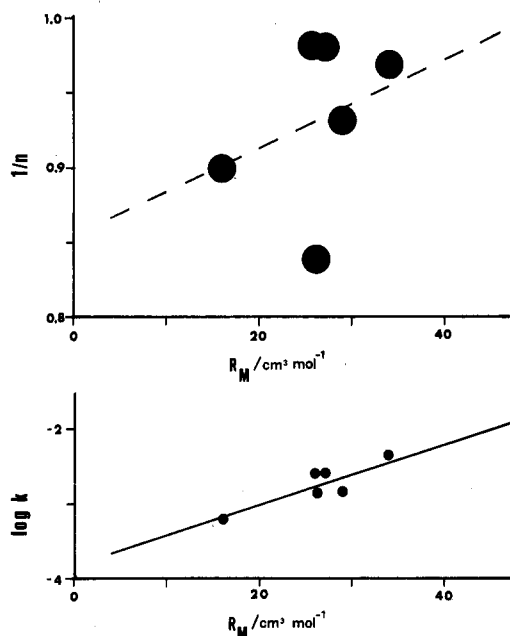


Figure 11. Regression of the Freundlich constants, in the forms $1/n$ and $\log k$, against adsorbate molar refractions, R_M , at 433 K. Ordinate scale of upper plot expanded to illustrate the magnitude of experimental scatter typical of that encountered in the correlations at other temperatures.

separations) can be forecast in advance.

Comparison of K_S at Zero Surface Coverage. The partition coefficients, $K_S/\text{cm}^3 \text{ m}^{-2}$, for all adsorbates were computed from the initial slopes of the isotherms via the relation

$$K_S = \left(\frac{qRT}{pS} \right)_{q \rightarrow 0} \quad (15)$$

The results are compared in Table V with the data determined with the same batch of Porapak Q at zero surface coverage. The self-consistency of the two sets of values is gratifying, particularly in view of the simplicity of the instrumentation and techniques with which the finite concentration ECP measurements were made.

Registry No. Porapak Q, 9043-77-0; hexane, 110-54-3; heptane, 142-82-5; cyclohexane, 110-82-7; benzene, 71-43-2; carbon tetrachloride, 56-23-5; acetone, 67-64-1.

LITERATURE CITED

- Hollis, O. L. *Anal. Chem.* **1966**, *38*, 309-316.
- Hollis, O. L. U.S. Patent 3 357 158, 1967.
- Hollis, O. L. U.S. Patent 3 458 976, 1969.
- Zado, F. M.; Fabecic, J. J. *Chromatogr.* **1970**, *51*, 37-44.
- Hollis, O. L. *J. Chromatogr. Sci.* **1973**, *11*, 335-342.
- Dressler, M.; Vespalec, R.; Janak, J. J. *Chromatogr.* **1971**, *59*, 423-428.
- Cassidy, R. M.; Hurteau, M. T.; Mislau, J. P.; Ashley, R. W. *J. Chromatogr. Sci.* **1976**, *14*, 444-447.
- Coppi, S.; Betti, A.; Blo, G.; Blighi, C. J. *Chromatogr.* **1983**, *267*, 91-99 and references therein.
- Lovkvist, P.; Jonson, J. A. Presented at the 15th International Symposium on Chromatography, Nuremberg, Oct 1984.
- Gough, T. A.; Simpson, C. F. J. *Chromatogr.* **1972**, *68*, 31-45.
- Castello, G.; d'Amatto, G. J. *Chromatogr.* **1980**, *196*, 245-254.
- Foris, A.; Lehman, J. G. *Sep. Sci.* **1969**, *4*, 225-241.
- Gvosdovich, T. N.; Kiselev, A. V.; Yashin, Ya. I. *Chromatographia* **1978**, *11*, 596-599.
- Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; Wiley: New York, 1982; Chapters XV and XVI.
- Laub, R. J.; Pecsok, R. L. *Physicochemical Applications of Gas Chromatography*; Wiley-Interscience: New York, 1978; Chapter 7.
- Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley: Chichester, England, 1979; Chapter 10.
- Cremer, E. *Monatsh. Chem.* **1961**, *92*, 112-115.
- Cremer, E.; Huber, H. F. *Angew. Chem.* **1961**, *73*, 461-465.
- Cremer, E.; Huber, H. F. In *Gas Chromatography 1961*; Brenner, N. Callen, J. E., Weiss, M. D., Eds.; Academic Press: New York, 1962; pp 169-182.
- Huber, J. F. K.; Keulemans, A. I. M. In *Gas Chromatography 1962*; van Swaay, M., Ed.; Butterworths: London, 1962; pp 26-35.

- (21) Glueckauf, E. J. *Chem. Soc.* **1947**, 1302-1308.
- (22) James, D. H.; Phillips, C. G. S. *J. Chem. Soc.* **1954**, 1066-1070.
- (23) Gregg, S. J.; Stock, R. In *Gas Chromatography 1958*; Desty, D. H., Ed.; Butterworths: London, 1958; pp 90-98.
- (24) Kiselev, A. V.; Yashin, Ya. I. *Gas-Adsorption Chromatography*; Bradley, J. E. S., Translator; Plenum: New York, 1969, Chapter IV.
- (25) Conder, J. R. In *Advances in Analytical Chemistry and Instrumentation*; Purnell, J. H., Ed.; Wiley-Interscience: New York, 1967; pp 209-270.
- (26) Conder, J. R. *J. Chromatogr.* **1969**, *39*, 273-281.
- (27) Conder, J. R. *Chromatographia* **1974**, *7*, 387-394.
- (28) Conder, J. R.; Purnell, J. H. *Trans. Faraday Soc.* **1968**, *64*, 3100-3111.
- (29) Conder, J. R.; Purnell, J. H. *Trans. Faraday Soc.* **1969**, *65*, 824-838.
- (30) Conder, J. R.; Purnell, J. H. *Trans. Faraday Soc.* **1969**, *65*, 839-848.
- (31) Gray, D. G.; Gullet, J. E. *Macromolecules* **1972**, *5*, 316-321.
- (32) Tremaine, P. R.; Gray, D. G. *Anal. Chem.* **1976**, *48*, 380-382.
- (33) Katz, S.; Gray, D. G. *J. Colloid Interface Sci.* **1981**, *82*, 326-338.
- (34) Köster, F.; Findenegg, G. H. *Chromatographia* **1982**, *15*, 743-747.
- (35) DeVault, D. J. *Am. Chem. Soc.* **1943**, *65*, 532-540.
- (36) Dreisbach, R. R. *Physical Properties of Chemical Compounds*; American Chemical Society: Washington, DC; Vol I (1955), II (1959), and III (1961).
- (37) Riddick, J. E.; Bunger, W. B. *Organic Solvents: Physical Properties and Methods of Purifications*, 3rd ed.; Wiley: New York, 1970; Vol. II.
- (38) Laub, R. J.; Martire, D. E.; Purnell, J. H. *J. Chem. Soc., Faraday Trans. 2* **1976**, *74*, 213-221.
- (39) Laub, R. J.; Purnell, J. H.; Williams, P. S.; Harblson, M. W. P.; Martire, D. E. *J. Chromatogr.* **1978**, *155*, 233-240.
- (40) Laub, R. J.; Pecok, R. L. *Physicochemical Applications of Gas Chromatography*; Wiley-Interscience: New York, 1978; Chapter 2.
- (41) Harblson, M. W. P.; Laub, R. J.; Martire, D. E.; Purnell, J. H.; Williams, P. S. *J. Phys. Chem.* **1979**, *83*, 1262-1268.
- (42) Ashworth, A. J.; Hooker, D. M. *J. Chromatogr.* **1979**, *174*, 307-313.
- (43) Cadogan, D. F.; Purnell, J. H. *J. Chem. Soc. A* **1968**, 2133-2137.
- (44) Purnell, J. H.; Vargas de Andrade, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 3585-3590.
- (45) Laub, R. J. *Anal. Chem.* **1984**, *56*, 2110-2115.
- (46) Laub, R. J. *Anal. Chem.* **1984**, *56*, 2115-2119.
- (47) Katz, S.; Gray, D. G. *J. Colloid Interface Sci.* **1981**, *82*, 318-325.
- (48) Milonjic, S. K.; Kopecki, M. M. *Chromatographia* **1984**, *19*, 342-346.
- (49) de Boer, J. H. *The Dynamical Character of Adsorption*; Clarendon: Oxford, 1953; p 49.
- (50) Johnson, J. F.; Barrall E. M., II *J. Chromatogr.* **1967**, *31*, 547-549.
- (51) Fuller, E. N. *Anal. Chem.* **1972**, *44*, 1747-1753.
- (52) Pollock, G. E.; O'Hara, D.; Hollis, O. L. *J. Chromatogr. Sci.* **1984**, *22*, 343-347.
- (53) Ali, S. G. A. H.; Purnell, J. H.; Williams, P. S. *J. Chromatogr.* **1984**, *302*, 119-133.
- (54) Brookman, D. J.; Sawyer, D. T. *Anal. Chem.* **1968**, *40*, 106-110.
- (55) Sawyer, D. T.; Brookman, D. J. *Anal. Chem.* **1968**, *40*, 1847-1853.
- (56) de Boer, J. H. *The Dynamical Character of Adsorption*; Clarendon: Oxford, 1953; pp 112-115.
- (57) Gearhart, H. L.; Burke, M. F. *J. Chromatogr. Sci.* **1973**, *11*, 411-417.
- (58) Kiselev, A. V.; Yashin, Ya. I. *Gas-Adsorption Chromatography*; Bradley, J. E. S., Translator; Plenum: New York, 1969; Chapter II.
- (59) Ross, S.; Olivier, J. P. *On Physical Adsorption*; Interscience: New York, 1964; Chapter 3.
- (60) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309-319.
- (61) Freundlich, H. *Colloid and Capillary Chemistry*; Methuen: London, 1926.
- (62) Dubinin, M. M. *Chem. Rev.* **1960**, *60*, 235-241.

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Deconvolution of Overlapping Chromatographic Peaks

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The use of multichannel chromatographic detectors that produce spectra characteristic of the eluents permits the deconvolution of partially overlapping chromatographic peaks without any assumptions about chromatographic peak shape or prior knowledge of the spectra of the individual compounds. With only weak assumptions about peak shape (e.g., nonnegativity of concentration), an error bound on the areas of the deconvolved peaks can be computed and the estimates of the spectra of eluting compounds improved. Examples are given of the application of a deconvolution method based on factor analysis of the spectra of eluting mixtures to GC/MS, LC/UV-vis, and GC/FTIR spectra. The method is embodied in a computer program that performs the deconvolution within a few minutes with a minimum of intervention by the user. For this deconvolution method to be successful, no more than three compounds can coelute at a given instant, and the periods when three compounds elute must be preceded and followed by periods where varying mixtures of just two compounds are eluting.

The information available in spectra produced by gas chromatography/mass spectroscopy (GC/MS), liquid chromatography with diode array detection (LC/UV-vis), or gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR) can be used to separate mathematically over-

lapping chromatographic peaks. This deconvolution is straightforward if the spectra of the compounds responsible for the peaks are known. Generally, they are not known, however, and in order to perform the deconvolution, it is necessary to make estimates of them from information in the experimental spectra. The contributions of each component to the experimental mixture spectra are then computed by least-squares fitting. The sequence of computed contributions vs. time describes the actual elution profiles of the components. A technique for estimating the component spectra of a series of binary mixtures was described by Lawton and Sylvestre (1) and applied to GC/MS data by Sharaf and Kowalski (2) and to LC/UV-vis data by Osten and Kowalski (3). A similar approach was taken by Chen and Hwang (4) and by Vandeginste et al. (5) to deal with three-component mixtures eluting from GC/MS and LC/UV-vis, respectively. Borgen and Kowalski (6) have described a method for placing bounds on the possible component spectra for three components that is generally applicable to chromatography. Gemperline (7) and Vandeginste et al. (8) have developed a method for deconvolution using iterative target transformation factor analysis, also generally applicable to chromatography, that has produced results comparable to those given here. In their method elution profiles are estimated first and the spectra computed from these.

In this paper, using an approach related to those mentioned above, estimates of the component spectra are first obtained from the information in the experimental spectra, and then