

CHROM. 20 453

REVERSIBILITY OF SOLVENT-INDUCED SURFACE MODIFICATION OF ALUMINA ADSORBENTS

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(First received October 26th, 1987; revised manuscript received March 1st, 1988)

SUMMARY

The adsorption isotherms and relevant thermodynamic data for the adsorption of four representative adsorbates establish that pre-washing a representative alumina adsorbent with *n*-hexane or benzene does not alter irreversibly its gas–solid chromatographic selectivity and that simple temperature conditioning is sufficient to restore it to its original state. Further, deviations in the zero surface coverage partition constants of any given adsorbate are no greater than the experimental uncertainties (largely owing to kinetic effects) that are usual in studies of this kind.

INTRODUCTION

Despite their widespread use early in the history of gas chromatography, the popularity of inorganic adsorbent packings (including various forms of activated carbon and silica, magnesia and alumina) has declined sharply in recent years, largely because of the introduction of porous organic polymer supports, *e.g.*, the Porapaks pioneered by Hollis¹. The latter materials exhibit column efficiencies that are appreciably higher than those generally observed with inorganic packings, owing mostly to improved peak symmetry, which is a function of surface homogeneity. The synthetic adsorbents also have the advantage of yielding overall faster times of analysis, particularly at reduced column temperatures.

However, the batchwise reproducibility of adsorbate retentions with polymer adsorbents remains far from satisfactory². Moreover, there are some analyses, especially those that involve fixed gases, that are still most easily accomplished with inorganic packings such as alumina and zeolites³. In addition, inorganic gas–solid

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chromatographic (GSC) adsorbents have the advantage that their selectivity can readily be modified by treatment with various salts, as demonstrated, *e.g.*, by Brookman and Sawyer^{4,5} using packed columns containing salt-coated silicas and, more recently, by De Zeeuw *et al.*⁶, who employed porous-layer open-tubular (PLOT) columns with a variety of adsorbents, including aluminas, silicas and molecular sieves coated with various dopants.

During studies of the GSC properties of aluminas, Al-Thamir *et al.*⁷ found that the packed-column GSC separation of the sixteen most commonly encountered light hydrocarbons could also be altered in remarkable ways simply by pre-treating the adsorbent with common hydrocarbon solvents, such as *n*-hexane or benzene. For example, the chromatographic characteristics of fully activated Alcoa F 20 neutral alumina were modified by slurring the adsorbent in a neat solvent at room temperature, followed by filtration, drying for 2 h at 383 K and then packing and conditioning in a stream of dry carrier gas at *ca.* 393 K. In addition, the effects of the solvent washing treatment were shown to persist even after continuous use of the columns for many hours at *ca.* 323 K, as evidenced by the constancy of raw retention times. [Adsorbents such as sheet silicate intercalates can, of course, catalyse the room-temperature interconversion of some organic compounds⁸, and it is conceivable that in the process of washing alumina with organic liquids the surface could have become contaminated with various products arising from catalytically induced reactions either of the solvent itself or of trace impurities contained within it (the irreversible adsorption of acetone by alumina due to the formation of the chelating agent diacetone alcohol is one well known example). The effects that volatile hydrocarbon solvents were shown to have on alumina adsorbents were nevertheless surprising.]

The latter work led us to consider recently whether the properties of alumina columns (packed or PLOT) could in fact be tailored to individual samples simply by prior injection of sufficient amounts of various volatile organic compounds (either neat or in admixture), that is, whether a means of *in situ* adjustment of the chromatographic selectivity of an adsorbent for specific analyses might be possible. Such an effect, if reproducible, could of course prove superior in terms of simplicity and ease of operation even to multiple-column switching systems. However, in order to achieve routine quantitative control over the selectivity of alumina packings in this way, the column treatment must be reversible such that the original selectivity of the adsorbent (*i.e.*, prior to solvent soaking) can be recovered, presumably simply by conditioning for a short period at elevated temperature. We have therefore undertaken, first, to assess the extent to which the original state of a representative sample of this adsorbent can be restored following its immersion in simple solvents and, second, to quantitate the effects that various volatile organic compounds exert on its chromatographic properties. We report in this paper our initial findings regarding the reversibility of the solvent-soaking process in terms of the reproducibility of the zero surface coverage partition constants and related thermodynamic parameters, as well as the finite surface coverage adsorption isotherms, of several representative adsorbates over the temperature range 333–373 K.

EXPERIMENTAL

The 60–80-mesh chromatography-grade alumina used throughout this study

was purchased from Kemika (Zagreb, Yugoslavia). It was washed with distilled water to remove any water-soluble contaminants and then filtered and dried overnight in an air oven at *ca.* 473 K. The sample was subsequently divided into four portions, one being left unmodified, while the remaining three were held for treatment with benzene or *n*-hexane as described below. Each portion was stored in a desiccator until used.

The GC system consisted of a Spectra-Physics Model 7100 research chromatograph with dual thermal conductivity detectors. A mercury manometer was connected to the column inlet for measurement of the inlet pressure, p_i . Control and monitoring of all other experimental variables requisite for high-precision GC measurements^{9,10} were then effected in the usual way¹¹. Hydrogen was used as the carrier gas throughout.

The alumina batches were treated separately with *n*-hexane and benzene as follows. The adsorbent was immersed in an excess of the liquid of interest in a PVC vessel, which was then left sealed for 10 days. Next, the packing was filtered, dried in an air oven just to the state of a free-flowing powder and then displaced by suction into a 50 cm × 0.6 cm I.D. stainless-steel column, 8 g of material typically being required. Each column was conditioned overnight at 473 K. In order to establish the reproducibility of the procedure, two of the lots of adsorbent were treated independently with *n*-hexane modifier, the third being treated with benzene.

The technique commonly referred to as elution by characteristic point (ECP) was employed to obtain the adsorption isotherms as described elsewhere^{12,13}. Briefly, separate injections of 1–5 mm³ of each liquid adsorbate were carried out. All peaks exhibited a diffuse tailing edge; data were taken only from those whose maxima were coincident with the diffuse edge of the tallest peak so as to avoid effects due to kinetic band broadening (*cf.*, Fig. 4 in ref. 12). The partial pressure, p , of adsorbate vapour in the gas phase was then calculated from the expression

$$p = (n_A s h R T) / (S_i F_c) \quad (1)$$

where n_A is the number of moles of adsorbate injected as calculated from its volume, density and molecular weight, s is the recorder chart speed, h is the height of the peak, R is the gas constant, T is the recorder chart speed, S_i is the chart area bounded only by the peak and F_c is the fully corrected carrier gas volume flow-rate. The amount of adsorbate adsorbed per gram of adsorbent, q , is then given by

$$q = (n_A S_A) / (m_S S_i) \quad (2)$$

where S_A is the chart area bounded by the diffuse profile of the chromatogram, the air peak and the peak height, and m_S is the mass of adsorbent in the column. The flow-rate was varied throughout the experimental work over the range 60–110 cm³ min⁻¹, depending on the adsorbate and the column temperature; no flow-rate-dependent changes in the patterns of adsorption were observed.

Partition constants, k_S (cm³ g⁻¹), were calculated from the initial slopes of the adsorption isotherms:

$$k_S = \left(\frac{qRT}{p} \right)_{q \rightarrow 0} \quad (3)$$

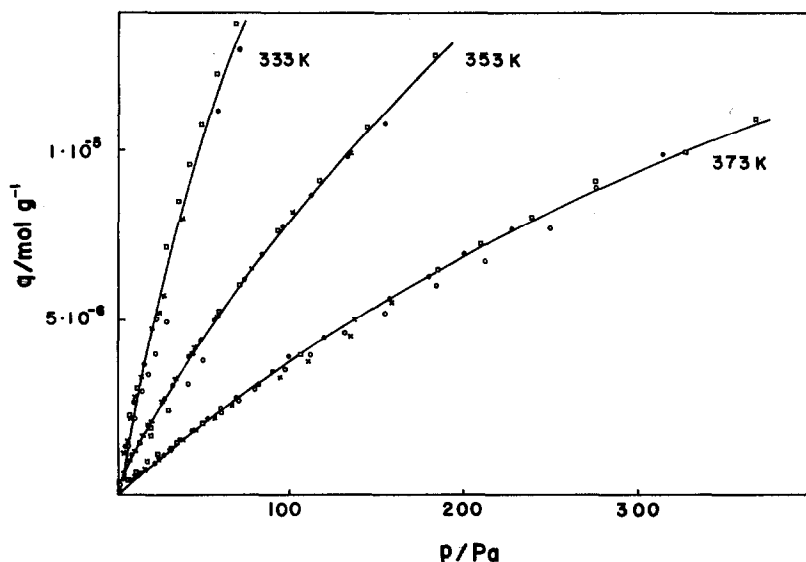


Fig. 1. Adsorption isotherms for benzene with untreated alumina and with alumina treated with *n*-hexane and benzene solvents. ○, untreated; ●, treated with *n*-hexane (first trial); □, treated with *n*-hexane (second trial); ×, treated with benzene. Solid curves: Freundlich isotherms (*cf.*, eqn. 4) calculated with best-fit variables in Table I.

[The data were taken simply in units of cubic centimetres per gram rather than per square metre, as the specific surface area, S ($\text{m}^2 \text{g}^{-1}$), of the adsorbent is hardly likely to change on exposure to *n*-hexane or benzene.] The relevant thermodynamic parameters of adsorption, *viz.*, enthalpies, entropies and Gibbs free energies per gram of adsorbent, were then calculated in the usual way from the inverse temperature dependence of $\log k_s$.

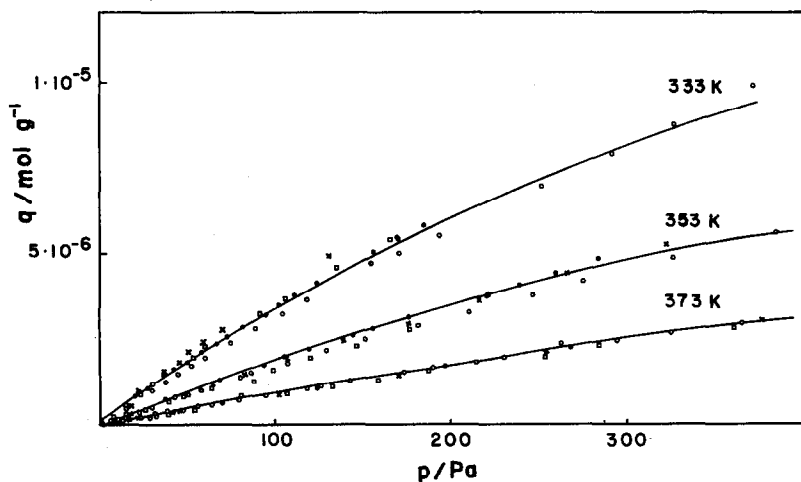


Fig. 2. As in Fig. 1; *n*-hexane adsorbate.

RESULTS AND DISCUSSION

Figs. 1 and 2 present the adsorption data for benzene and *n*-hexane adsorbates with all batches of treated and untreated alumina examined (those for cyclohexane and chloroform were very similar in appearance and are therefore not shown). The solid curves are the isotherms generated with the best-fit constants of the Freundlich expression¹⁴, the logarithmic form of which is

$$\log q = \log k + (1/n) \log p \quad (4)$$

where q and p are as defined above (p in Pa) and k and n are temperature-dependent variables whose values vary from one adsorbate to another. The Freundlich constants for all adsorbates are given in Table I.

It is immediately evident that, apart from the experimental scatter commonly encountered in studies of this kind (owing largely to non-equilibrium kinetic effects), there are in fact no discernible differences between the adsorption isotherms obtained with untreated alumina and alumina that was treated and then reconditioned. That is, changes in the adsorptive properties of alumina induced by solvent soaking with either *n*-hexane or benzene appear to be reversible insofar as can be ascertained from the adsorbate finite-concentration adsorption isotherms.

We also found that the values of k and n for any given adsorbate fluctuated randomly about the respective averages, *i.e.*, deviations from the mean values obtained with one batch of adsorbent were not systematically different from those found with any other. Moreover, the partition constants calculated from the finite-concentration data and eqn. 3 were in good agreement with those obtained from zero surface coverage experiments, which establishes that the retentions were governed by adsorbate-adsorbent interactions free from lateral adsorbate-adsorbate effects. In addition, the k_s for a given adsorbate were constant to within $\pm 7\%$ from one batch of alumina (treated or otherwise) to another. Even those for chloroform adsorbate, which gave the largest variations (probably owing to specific interactions, *e.g.*, hydrogen bonding) exhibited only random fluctuations about a mean value at each temperature. Hence, the variations in the adsorbate k_s with any individual adsorbent can be said overall to be a consequence of experimental uncertainties (chiefly non-equilibrium effects as mentioned previously), rather than being due to any permanent effects resulting from treatment with a particular solvent.

Table II presents the enthalpies of adsorption calculated from the slopes of the

TABLE I
BEST-FIT FREUNDLICH CONSTANTS FOR VARIOUS ADSORBATES WITH ALUMINA ADSORBENT AT 333-373 K

Adsorbate	$T_b(K)$	333 K		353 K		373 K	
		$10^6 k$	$1/n$	$10^6 k$	$1/n$	$10^6 k$	$1/n$
<i>n</i> -Hexane	342.2	5.5 ± 0.3	1.12 ± 0.01	2.3 ± 0.2	1.08 ± 0.02	1.24 ± 0.08	1.97 ± 0.01
Cyclohexane	354.6	3.6 ± 0.3	1.10 ± 0.01	1.7 ± 0.1	1.08 ± 0.02	0.90 ± 0.1	1.08 ± 0.01
Benzene	353.3	36.0 ± 3	1.21 ± 0.02	16.0 ± 1	1.20 ± 0.02	6.15 ± 0.06	1.13 ± 0.01

TABLE II

HEATS OF ADSORPTION, $-\Delta H_s$, OF VARIOUS ADSORBATES WITH UNTREATED ALUMINA AND WITH RECONDITIONED ALUMINA FOLLOWING TREATMENT EITHER WITH BENZENE OR *n*-HEXANE SOLVENTS

Solvent	$-\Delta H_s(\text{kJ mol}^{-1})$			
	<i>n</i> -Hexane	Cyclohexane	Benzene	Chloroform
None	30 ± 1	30 ± 3	39 ± 5	47 ± 4
<i>n</i> -Hexane*	35 ± 3	33 ± 1	44 ± 3	46 ± 2
	38 ± 1	32 ± 1	48 ± 1	
Benzene	38 ± 1	34 ± 1	43 ± 3	48 ± 1
Average	36 ± 6	32 ± 3	44 ± 6	47 ± 8

* Replicate trials carried out with separate batches of alumina.

van't Hoff plots of the adsorbate retentions at zero surface coverage. As shown, replicate measurements for each solute were precise to no worse than $\pm 5 \text{ kJ mol}^{-1}$, while the overall average precision was $\pm 2 \text{ kJ mol}^{-1}$. The averaged enthalpies are also presented, together with the respective 95% confidence intervals. These data indicate that there is no statistically significant deviation that can be linked to any one batch of adsorbent, which substantiates the conclusion reached earlier that the treatment of alumina with volatile hydrocarbon solvents such as *n*-hexane and benzene alters its chromatographic selectivity in a reversible way.

ACKNOWLEDGEMENT

Support provided for this work in part by the U.S. Department of Energy Office of Basic Energy Sciences (analytical considerations; zero surface coverage studies) and by the National Science Foundation (finite-concentration work) is gratefully acknowledged.

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