CHROM. 9548

STUDIES OF CHROMATOGRAPHIC PACKINGS COMPRISING CHEMICALLY BONDED PHASES OBTAINED FROM POROUS GLASS BEADS

I. SORPTION PROPERTIES AND SURFACE HETEROGENEITY

J. GAWDZIK and Z. SUPRYNOWICZ

Department of Physical Chemistry, Institute of Chemistry UMCS, Nowotki 12, 20031 Lublin (Poland)

and

M. JARONIEC

Department of Theoretical Chemistry, Institute of Chemistry UMCS, Nowotki 12, 20031 Lublin (Poland)

(Received June 14th, 1976)

SUMMARY

The adsorption properties and surface heterogeneity of chromatographic packings comprising chemically bonded phases obtained from controlled-pore glass beads have been studied. The bonded phases were prepared by reaction of glass beads with trichlorooctadecylsilane, trichlorophenylsilane, dichloro(2-cyanoethyl)-methylsilane or (3-aminopropyl)triethoxysilane. Adsorption isotherms and energy-distribution functions have been calculated for benzene and *n*-hexane on the chemically bonded phases.

INTRODUCTION

The past five years have seen a tremendous growth in the popularity and utilization of bonded phases[1]. A number of reports have been devoted to these chromatographic packings[2–4]. The latest study by Rehák and Smolková[5] indicates the continuing employment of such packings. Bonded phases are particularly popular as packings for liquid chromatography[2]. Most of the bonded phases used so far were prepared on the basis of diatomaceous supports[6,7], silica gels[8], aluminium oxides and controlled surface-porosity supports and adsorbents[5,9,10]. These studies concentrated on the analytical and preparative aspects.

In the present paper, particular consideration will be given to physicochemical studies of chemically bonded phases prepared on glass beads of controlled porosity. Glass beads of controlled porosity were used, which were prepared in our Department[11,12]. The properties of the beads were the subject of detailed discussion in our previous paper[12]. The physicochemical investigations were carried out by the method previously used[12–14].

Porous glass beads have been used chiefly for the preparation of packings employed in affinity chromatography[15-17]. Some remarks on the application of modified porous glass in gas chromatography were made by Wolf and Heyer[18]. However, these workers used glass beads having a microporous structure which considerably limited their application. Interesting spectroscopic investigations of packings prepared on porous glass by reaction with trichlorooctadecylsilane (ODS) and (3-aminopropyl)-triethoxysilane (NHS) phases were recently carried out by Lynn and Filbert[19]. However, more extensive chromatographic studies of the packings obtained were not conducted.

EXPERIMENTAL

Materials

The controlled-pore glass beads used were previously described[12]. The spherical adsorbent (particle diameter, 0.15–0.20 mm) had a specific surface area of 71.5 m²/g (measured by nitrogen adsorption), a pore radius of 130 Å and a total porosity of 0.64 cm³/g (obtained by use of a mercury porosimeter). This adsorbent was prepared in our Department.

The reagents ODS, trichlorophenylsilane (PhS), dichloro(2-cyanoethyl)methyl-silane (CNS) and NHS were obtained from Pierce, Rotterdam, The Netherlands. Hexamethyldisilazane (purum, 98 %) was obtained from Fluka, Buchs, Switzerland. Toluene was analytical reagent grade, obtained from Polskie Odczynniki Chemiczne, Gliwice, Poland. It was stored over silica gel. Benzene, acetone and methanol (Polskie Odczynniki Chemiczne) were analytical reagent grade and were used without further purification. *n*-Hexane (chemically pure, 99 %) was obtained from Reachim, Moscow, U.S.S.R.

Preparation of the chemically bonded packings

The chemically bonded stationary phases were prepared in the following manner. 10 g of controlled-pore glass beads (this adsorbent will be denoted by G) were dried in a laboratory oven at 200°C for 24 h. The hot adsorbent was then placed into a PTFE-lined autoclave (volume, *ca.* 100 cm³) containing 50 cm³ of a 0.5 *M* solution of organosilane reagent in dry toluene. The autoclave was closed and placed in the oven at 100°C for 10 h. On completion of the reaction, the autoclave was cooled to room temperature. The excess of organosilane solution was decanted off and the packings were washed five times by decantation in benzene. The packings were then extracted in a Soxhlet extractor by using benzene, acetone and methanol. Each extraction process required 6 h. Finally, the packings were dried at room temperature and packed into the chromatographic columns. The reactions of the adsorbent G with ODS, PhS and CNS were carried out in this way. In the case of NHS, prior to the bonding reaction, the adsorbent was conditioned to a relative humidity of 15% by placing it over a saturated solution of lithium chloride in a desiccator for 24 h.

Silanization of chemically bonded packings

Before silanization, 10 g of packing were dried in the oven at 110°C for 2 h. Then the packing was placed in 50 cm³ of a 5% v/v solution of hexamethyldisilazane in dry toluene contained in the autoclave. The autoclave was placed in the oven at

100 °C for 10 h. On completion of the reaction the packing was washed five times by decantation with dry benzene and then with methanol. The packing was allowed to stand in methanol for 1 h, whereupon the methanol was filtered over a glass frit and the packing was dried at room temperature. Silanized packings will be denoted by s, whereas unsilanized packings will be denoted by ns.

Chromatographic measurements

The measurements were carried out on a Chromatron GCHF 18.3 gas chromatograph equipped with a thermal conductivity detector. Hydrogen, purified by use of a filter containing molecular sieve 5A, was used as the carrier gas at a flow-rate of 50 cm³/min. A glass column (100 cm × 3 mm I.D.) containing the packing was conditioned with carrier gas at 473 K for 12 h. The measurements were made at 343, 358 and 373 K. The stability of the column temperature was ± 0.1 K. The injector temperature was 473 K. The column detector was calibrated by injecting various amounts of adsorbate by means of 1-, 10- and 50-μl Hamilton microsyringes into the column containing the partition packing (10% E-30 on siliconized Diatomite C, 100–120 mesh; Pye Unicam, Cambridge, Great Britain).

The experimental retention volume, $V_{N,t}(p)$, versus p data were obtained by the peak-maxima elution method[20] for the following systems:

(1) benzene on ODS–ns–G and ODS–s–G (Figs. 1 and 2)
(2) n-hexane on ODS–ns–G and ODS–s–G (Figs. 3 and 4)
(3) benzene on PhS–ns–G and PhS–s–G (Figs. 5 and 6)
(4) benzene on CNS–ns–G and CNS–s–G (Figs. 7 and 8)
(5) benzene on NHS–ns–G and NHS–s–G (Figs. 9 and 10)

For example, ODS–ns–G denotes unsilanized packing obtained from adsorbent G and organosilane ODS. In Figs. 1–10 adsorption isotherms are also presented; these were calculated according to the equation reported previously[12,13].
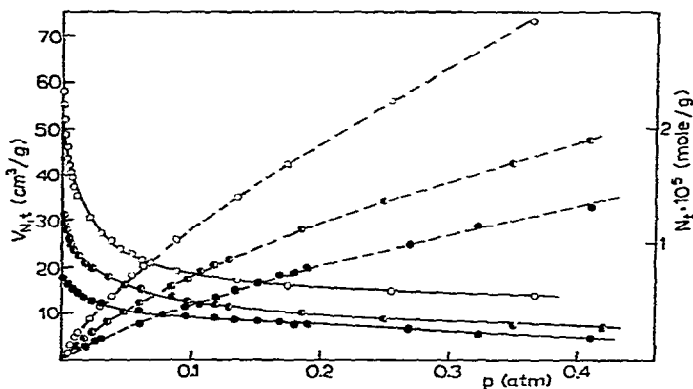

Fig. 1. Adsorption of benzene on ODS–ns–G. The solid lines denote the functions $V_{N,t}(p)$, and the broken lines denote the adsorption isotherms, at different temperatures: ○, 343; ◑, 358; ●, 373 K.
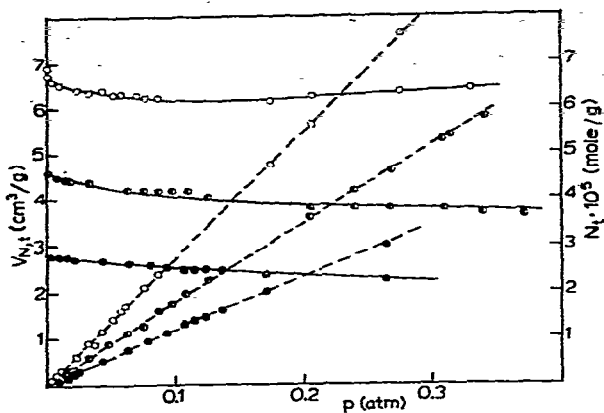
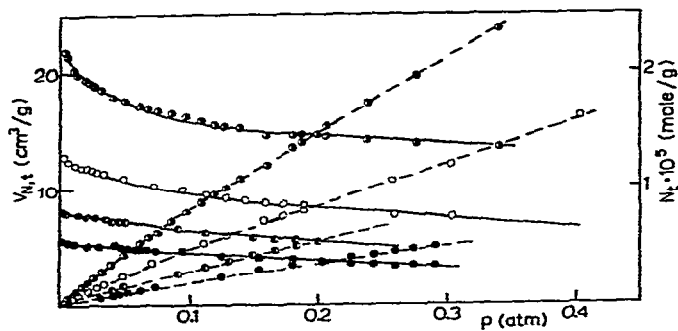Fig. 2. Adsorption of benzene on ODS–s–G. Details as in Fig. 1.

Fig. 3. Adsorption of *n*-hexane on ODS–ns–G. Details as in Fig. 1; ◐, data at 328 K.
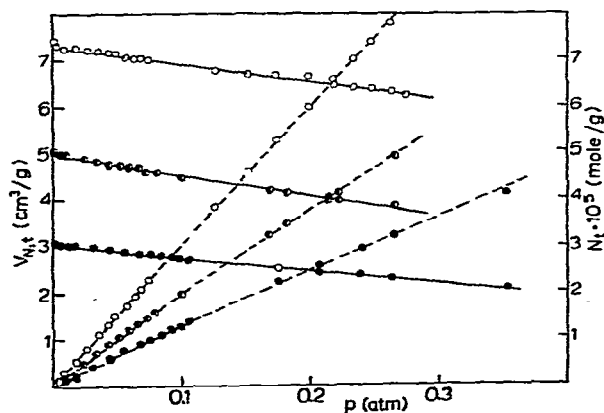
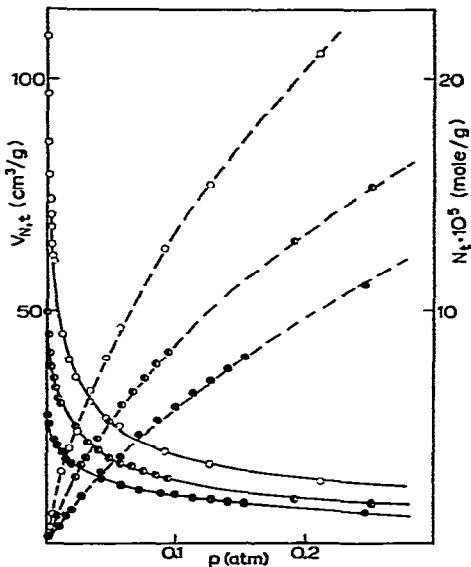Fig. 4. Adsorption of *n*-hexane on ODS–s–G. Details as in Fig. 1.

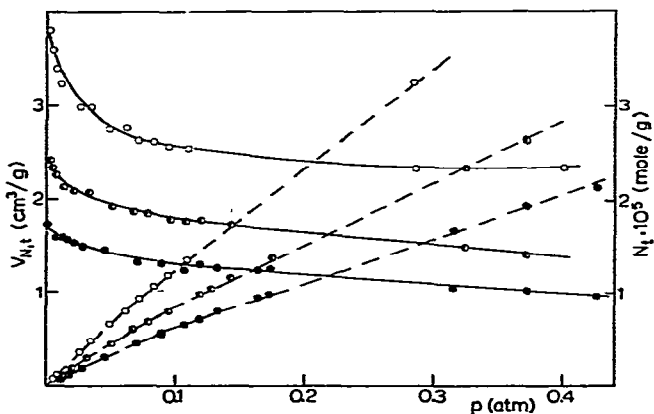Fig. 5. Adsorption of benzene on PhS–ns–G. Details as in Fig. 1.

Fig. 6. Adsorption of benzene on PhS–s–G. Details as in Fig. 1.
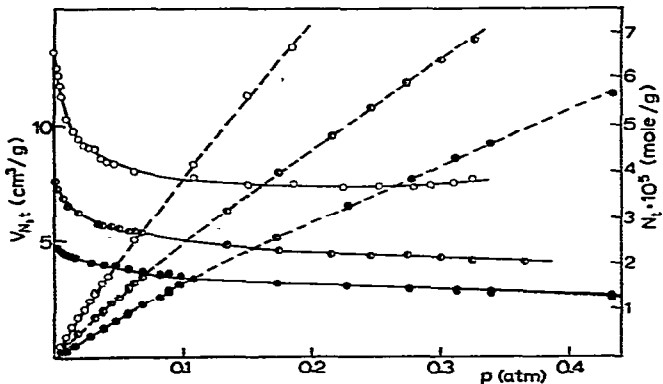

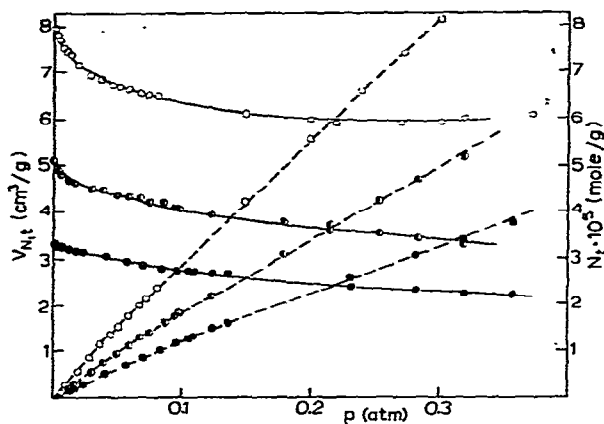Fig. 7. Adsorption of benzene on CNS–ns–G. Details as in Fig. 1.

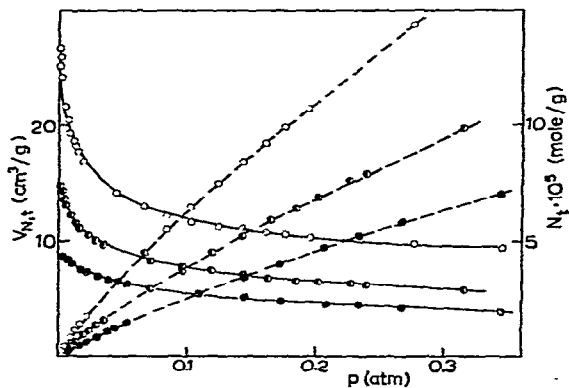Fig. 8. Adsorption of benzene on CNS–s–G. Details as in Fig. 1.

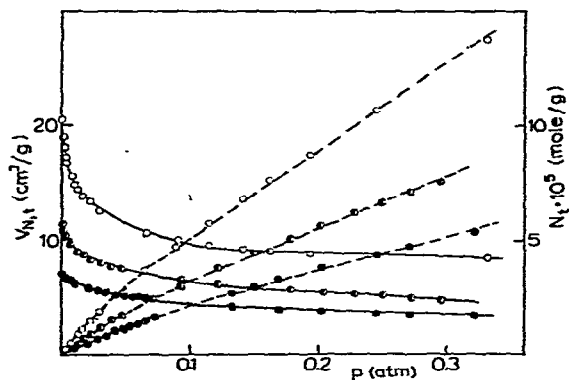Fig. 9. Adsorption of benzene on NHS–ns–G. Details as in Fig. 1.

Fig. 10. Adsorption of benzene on NHS–s–G. Details as in Fig. 1.

RESULTS AND DISCUSSION

The experimental functions $V_{N,t}(p)$ in Figs. 1–10 were approximated according to the equation used previously[12,13]

$$V_{N\,t}(p) = \exp\left(\sum_{t=0}^{m} B_t\, p^t\right) \tag{1}$$

where p is the adsorbate pressure and B_t $(i = 1, 2, ..., m)$ are approximation coefficients. The parameters $\exp(B_0)$ and $B_1 RT \exp(B_0)$ characterizing the investigated systems are summarized in Table I: these parameters are related to the virial coeffi-

TABLE I

PARAMETERS FROM THE APPROXIMATION IN EQN. 1 WHICH CHARACTERIZE THE INVESTIGATED SYSTEMS

System	Temperature (°K)	m	$S \cdot 10^6$ (l^2/g^2)	$\exp(B_0) \cdot 10^3$ (l/g)	$-B_1 RT \exp(B_0)$ ($l^2/mole \cdot g$)	$\dfrac{-\exp(B_0)}{RTFB_1} \cdot 10^5$ ($mole/g$)
Benzene–ODS–ns–G	343	7	29.28	55.70	91.32	4.18
	358	7	6.47	30.57	29.37	3.95
	373	7	0.62	17.46	9.46	4.05
Benzene–ODS–s–G	343	7	0.021	6.82	1.171	4.89
	358	7	0.014	4.62	0.445	5.98
	373	7	0.004	2.83	0.114	8.79
n-Hexane–ODS–ns–G	328	6	0.624	21.98	5.521	10.67
	343	6	0.210	12.68	1.401	14.35
	358	6	0.028	7.92	0.502	15.59
	373	6	0.047	5.31	0.342	10.36
n-Hexane–ODS–s–G	343	6	0.016	7.39	0.114	59.79
	358	6	0.062	5.00	0.045	69.14
	373	6	0.002	3.10	0.143	9.55
Benzene–PhS–ns–G	343	7	305.3	97.9	858.1	1.41
	358	7	15.36	48.8	254.5	2.42
	373	7	2.36	26.9	73.5	4.66
Benzene–PhS–s–G	343	5	0.046	3.81	36.00	13.20
	358	5	0.019	2.47	18.27	17.13
	373	5	0.010	1.71	7.79	28.05
Benzene–CNS–ns–G	343	6	1.25	12.55	7.56	2.61
	358	6	0.14	7.48	3.05	2.32
	373	6	0.02	4.73	0.99	2.87
Benzene–CNS–s–G	343	7	0.023	7.98	1.782	4.34
	358	7	0.025	5.07	1.045	3.03
	373	7	0.009	3.33	0.206	6.70
Benzene–NHS–ns–G	343	7	3.02	26.4	29.09	2.40
	358	7	0.35	15.0	10.67	2.11
	373	7	0.03	9.0	3.03	2.69
Benzene–NHS–s–G	343	7	2.50	19.49	19.17	1.98
	358	7	0.22	11.13	7.52	1.65
	373	7	0.03	6.89	3.03	1.57

cients and the monolayer capacity[12,13]. In this table the sum of the squared deviations, S, is also given. For the purpose of calculating the pre-exponential factor of Henry's constant, K, and the average adsorption energy, $\bar{\varepsilon}$, we approximated the experimental B_0 values by using the following equation[13]:

$$B_0 - \ln T = \ln \left(\frac{FRN_m}{K} \right) + \frac{\bar{\varepsilon}}{R} \cdot (1/T) \qquad \cdot (2)$$

where N_m is the monolayer capacity and F is the James–Martin factor.

The experimental relations $(B_0 - \ln T)$ *versus* $(1/T)$, evaluated for all the investigated systems, are presented in Fig. 11. The parameters K and $\bar{\varepsilon}$ calculated from the slopes and intercepts of the straight lines in Fig. 11 are summarized in Table II. Using the values of K from Table II, we calculated the energy distribution function for each system according to the following equation[12,13]:

$$\chi(\varepsilon) = \frac{-p^2}{F \ln 2 \, (RT)^2} \left(\sum_{i=1}^{m} i \, B_i \, p^{i-1} \right) \exp \left(\sum_{i=0}^{m} B_i \, p^i \right) \qquad (3)$$

where

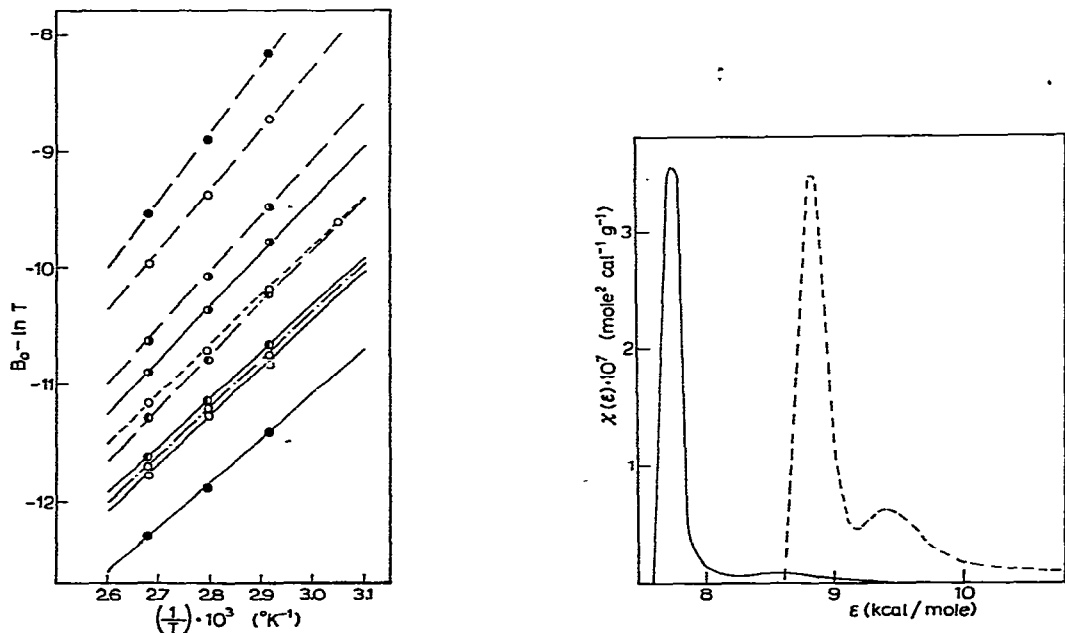$$\varepsilon \doteq RT \ln (K \ln 2/p) \qquad (4)$$

Fig. 11. Graphs of the experimental functions $(B_0 - \ln T)$ *versus* $(1/T)$ for adsorption of benzene on unsilanized packings (— — —) and on silanized packings (————), for *n*-hexane on ODS–ns–G (-------) and on ODS–s–G (— · — ·). Bonded phases: ○, ODS; ●, PhS; ◑, CNS; ◐, NHS.

Fig. 12. Energy distribution functions calculated according to eqn. 3 for benzene on ODS–ns–G (-------) and ODS–s–G (————) at 358 K.

TABLE II

PARAMETERS CHARACTERIZING THE ADSORPTION OF BENZENE AND n-HEXANE ON THE CHEMICALLY BONDED PHASES

Adsorbent	Adsorbate	$N_m \cdot 10^5$ (mole/g)	$\bar{\varepsilon}$ (kcal/mole)	$K \cdot 10^{-4}$ (atm^{-1})
ODS–ns–G	Benzene	4.06	10.6	9.1
ODS–ns–G	n-Hexane	12.74	8.2	3.0
ODS–s–G	Benzene	6.61	8.1	3.3
ODS–s–G	n-Hexane	46.16	8.1	3.0
PhS–ns–G	Benzene	2.83	11.8	15.8
PhS–s–G	Benzene	19.46	7.6	7.1
CNS–ns–G	Benzene	2.60	9.1	2.6
CNS–s–G	Benzene	4.69	8.3	2.1
NHS–ns–G	Benzene	2.40	9.9	3.9
NHS–s–G	Benzene	1.73	9.6	2.4

The distribution functions, $\chi(\varepsilon)$, presented in Figs. 12–15, were calculated only in the energy range corresponding to the experimental range of adsorption pressures in which the linearity of the chromatographic detector is preserved. Therefore the distribution functions for the systems benzene–CNS–G (Fig. 14) and benzene–NHS–G (Fig. 15) do not show distinct main peaks as is the case in the systems benzene–ODS–G and benzene–PhS–G (Figs. 12 and 13). For the first two systems, measurements of $V_{N,t}(p)$ at higher pressures would be necessary in order to obtain the main maxima in the distribution functions $\chi(\varepsilon)$. This information, however, is not of great importance, because we dispose the values of average adsorption energies given in Table II.

Of most interest are the courses of the distribution functions in the region of chromatographic adsorbate pressures. In this case we may attempt to draw some conclusions. All of the distribution functions (see Fig. 16) show two maxima. The main maximum seems to correspond to the interaction energy of the characteristic functional groups of the given packing with the adsorbate (these maxima are only visible in Figs. 12 and 13), whereas the second maximum corresponds to the bonded hydroxyl groups present on the surface of the packing. The existence of these groups on the surface of porous glass beads was indicated by the main peak in the distribution function $\chi(\varepsilon)$ calculated for the system benzene–G (Fig. 8 in ref. 12). Also, a considerable flattening of the distribution functions is visible in the region of high adsorption energies in the case of unsilanized packings. This energy range corresponds to the energies of the second maxima in the function $\chi(\varepsilon)$ for adsorbent G (Fig. 8 in ref. 12). These energies may be correlated with the interaction energies of the adsorbate molecules with free hydroxyl groups present on the adsorbent surface. This interpretation is still highly qualitative and we are conducting other studies to justify it. From a theoretical point of view, the energy of a particular maximum in the function $\chi(\varepsilon)$ cannot be attributed to functional groups on the surface, because these groups are involved in interactions and we have already obtained averge adsorption energies. It should also be borne in mind that the method used is approximate and gives information about the most distinctive effects characterizing a given system. It is of interest to compare unsilanized packings with silanized ones (Fig. 16). The distribution functions $\chi(\varepsilon)$ for the unsilanized packings cover a much wider range of energy
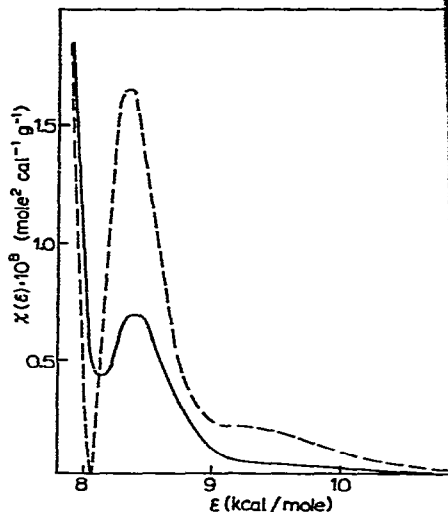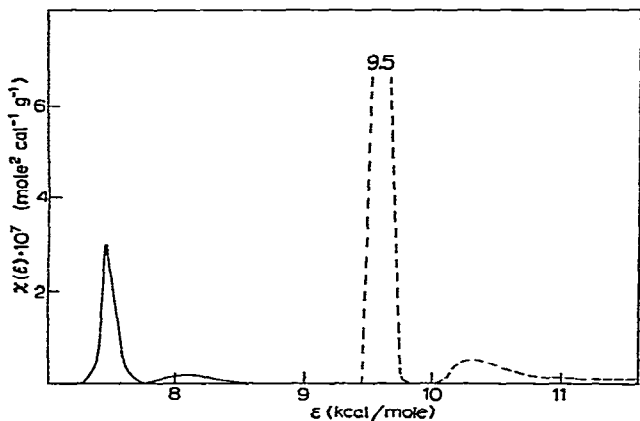
Fig. 13. Energy distribution functions for benzene on PhS–ns–G (---------) and PhS–s–G (————) at 358 K.

Fig. 14. Energy distribution functions for benzene on CNS–ns–G (---------) and CNS–s–G (————) at 358 K.
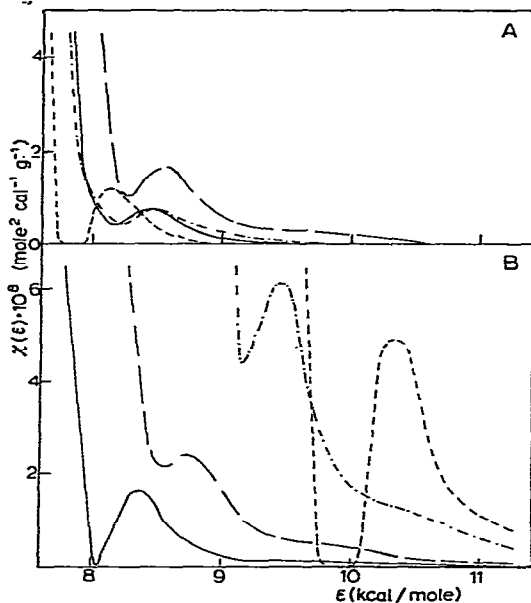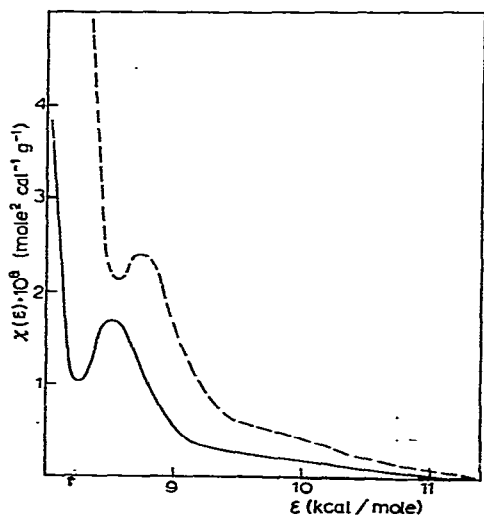

Fig. 15. Energy distribution functions for benzene on NHS–ns–G (---------) and NHS–s–G (————) at 358 K.

Fig. 16. Comparison of the energy distributions for different packings at 358 K: A, silanized packings; B, unsilanized packings. Bonded phases: (---------), PhS; (— · — ·), ODS; (— — —), NHS; (————), CNS.
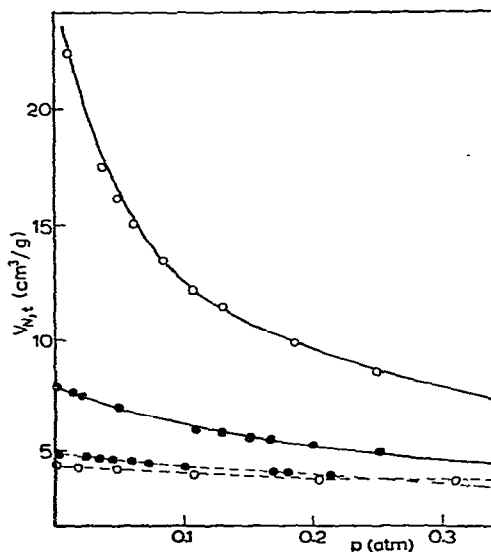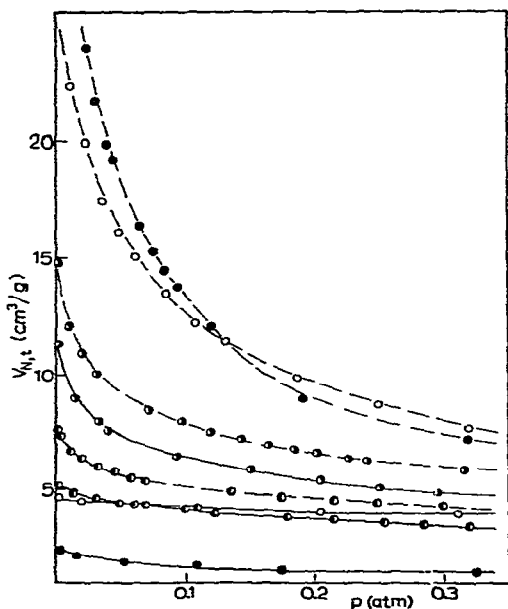
Fig. 17. Comparison of the functions $V_{N,t}(p)$ for adsorption of benzene on different packings at 358 K: --------, unsilanized packings; ——————, silanized packings. Phases as in Fig. 11.

Fig. 18. Comparison of the functions $V_{N,t}(p)$ for benzene ( ) and n-hexane (●) on ODS–ns–G (——————) and ODS–s–G (----------) at 358 K.

than the functions for the silanized packings. This gives information about the tightness of the surface coverage by the functional groups of the organosilanes. Silanization causes a further large decrease in the number of hydroxyl groups on the surface, and is reflected in the considerable decrease in the second peak and the earlier extinction of $\chi(\varepsilon)$ in the region of high energies (Fig. 16A). The silanization also causes differences between the distribution functions to disappear (Fig. 16A), the functions becoming more alike and lying in similar ranges of adsorption energy.

The distribution functions for the same kind of packing, silanized or unsilanized, can also be compared. The investigated packings can be divided into two groups: the first group includes the packings based on the CNS and NHS phases, whereas the second contains the packings based on the ODS and PhS phases. The distribution functions for silanized and unsilanized packings in the first group show only small differences (Figs. 14 and 15). In this case silanization only slightly changes the properties of these packings. However, in the second group (Figs. 12 and 13) silanization results in radical changes in properties. This confirms that the unsilanized packings in the second group contain a great number of hydroxyl groups which considerably reduce the effectiveness of these packings. In the case of the packing on the PhS phase, the formation of new hydroxyl groups is also probable (in place of chlorine atoms). This is demonstrated by the distribution $\chi(\varepsilon)$ presented in Fig. 13 where it can be seen that the very large second maximum for the unsilanized packing decreases after silanization. This is also borne out by the adsorption energy $\bar{\varepsilon}$ given in Table II. Generally, it can be concluded that the organosilanes CNS and NHS reacted to a higher

extent with the surface than did ODS and PhS. This behaviour is mainly connected with the steric effects.

Fig. 17 presents a comparison of the functions $V_{N,t}(p)$ for benzene on the packings at 358 K. This provides information about the sequence of benzene elution on the particular packings. The extrapolated retention volumes can be correlated with the adsorption energies. Taking into account the adsorption energies $\bar{\varepsilon}$ from Table II and the sequences of the curves in Figs. 11, 16 and 17, the packings can be arranged in the following order of elution of benzene: PhS–ns–G > ODS–ns–G > NHS–ns–G > NHS–s–G > CNS–ns–G > CNS–s–G > ODS–s–G and Phs–s–G. This order gives information about the direction of the change in adsorption energy of benzene, and indicates that silanization thoroughly changes the packings comprising the PhS and ODS phases. A comparison of the functions $V_{N,t}(p)$ for benzene and n-hexane on the packings with the ODS phase is interesting, because in the case of unsilanized ODS lower retention volumes are observed for hexane than benzene, whereas the reverse effect is observed in the case of the silanized packing (Fig. 18).

In this paper the behaviour of the chromatographic systems towards benzene have been studied and characterized. Further studies of this kind will be conducted for other adsorbates by using a simplified version of the above method.

REFERENCES

1 E. Grushka (Editor), *Bonded Stationary Phases in Chromatography*, Ann Arbor. Sci. Publ., Ann Arbor, Mich., 1974.
2 D. C. Locke, *J. Chromatogr. Sci.*, 11 (1973) 120.
3 R. E. Majors, *Int. Lab.*, July–August (1972) 25.
4 R. E. Majors, *Int. Lab.*, November–December (1975) 11.
5 V. Rehák and E. Smolková, *Chromatographia*, 9 (1976) 219.
6 W. A. Aue and C. R. Hastings, *J. Chromatogr.*, 42 (1969) 319.
7 C. R. Hastings, W. A. Aue and J. M. Augl, *J. Chromatogr.*, 53 (1970) 487.
8 R. E. Majors and M. J. Hopper, *J. Chromatogr. Sci.*, 12 (1974) 767.
9 J. J. Kirkland and J. J. DeStefano, *J. Chromatogr. Sci.*, 8 (1970) 309.
10 J. J. Kirkland, *J. Chromatogr. Sci.*, 9 (1971) 206.
11 J. Gawdzik, *Ph. D. Dissertation*, M. Curie-Skłodowska University, Lublin, 1976.
12 J. Gawdzik, Z. Suprynowicz and M. Jaroniec, *J. Chromatogr.*, 121 (1976) 185.
13 Z. Suprynowicz, M. Jaroniec and J. Gawdzik, *Chromatographia*, 9 (1976) 161.
14 Z. Suprynowicz and M. Jaroniec, *J. Chromatogr.*, 117 (1976) 11.
15 G. P. Royer and J. P. Andrews, *Polym. Preprints*, 13 (1972) 848.
16 G. P. Royer and J. P. Andrews, *J. Biol. Chem.*, 248 (1973) 1807.
17 G. P. Royer and J. P. Andrews, *J. Macromol. Sci.*, A7 (1973) 1167.
18 F. Wolf and W. Heyer, *J. Chromatogr.*, 35 (1968) 489.
19 M. Lynn and A. M. Filbert, in E. Grushka (Editor), *Bonded Stationary Phases in Chromatography*, Ann Arbor Sci. Publ., Ann Arbor, Mich., 1974, pp. 1–11.
20 J. F. K. Huber and R. G. Gerritse, *J. Chromatogr.*, 58 (1971) 137.