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SELECTIVITY OF NUCLEOSIL 10 NH₂ AS AN ADSORBENT IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Net retention volumes per gram of Nucleosil 10 NH₂ have been measured for a large number of mono- and disubstituted benzene derivatives and of polycyclic aromatic hydrocarbons, using *n*-hexane, dichloromethane and a mixture of both as eluents at 25°.

The retention data are interpreted in terms of the semi-empirical adsorption model, developed by Snyder for bare adsorbents, using octadecylsilylsilica as a reference adsorbent. The effects of the bound monomers on adsorbent deactivation, solute and eluent localization, change of the charge distribution in the solute molecule and adsorption mode of the solute are evaluated and discussed in terms of donor–acceptor interaction (including hydrogen bonding).

INTRODUCTION

Recent investigations on solute retention behaviour on bonded phases[1,2] have shown that the adsorption model of Snyder[3] is a valuable tool for the characterization of the adsorptive properties of these interesting adsorbents. As this model was developed to describe adsorption on bare adsorbents, it can be expected that its applicability to adsorption equilibria on chemically modified silicas will be restricted to silicas covered by moderate amounts of bound monomers. Further, the model does not account for solute–eluent interactions and hence it is not suitable for describing solute adsorption from the very polar solvents commonly used in reversed-phase and ion-pair chromatography. Finally, it can only predict the retention data of flatly adsorbed solute molecules. Despite these restrictions, it is a reliable guide for selecting and optimizing separation systems in high-performance liquid chromatographic (HPLC) practice.

The aim of this work was to evaluate (1) the change in the adsorptive properties of silica as a result of the reaction with the monomers and (2) the specific contribution of solute–monomer interactions to solute retention.

In order to distinguish both contributions, an appropriate reference bonded phase is required, and in this work octadecylsilylsilica (ODS-silica) with a relatively

low surface concentration of ODS groups was used. In order to exclude hydrophobic interaction effects, *n*-hexane, dichlomethane and a mixture of both were used as eluents. Hence, the application of Snyder's model to retention data on ODS-silica yields model parameters that characterize the adsorptive properties of silica covered by apolar monomers in such an amount that all reactive silanol groups are eliminated and only free silanol groups are present on the silica surface beneath the ODS bristles, and flat adsorption of solutes is not restricted by the anchored monomers up to solute molecular diameters of about 9 Å (*e.g.*, coronene).

This concept considerably facilitates the interpretation of solute retention on a given polar monomeric bonded phase, as a discrepancy between the value of any parameter of the polar bonded phase and of ODS-silica is related to a particular adsorptive property of the polar bonded phase in question. With respect to N-cyanoethyl-N-methylaminosilica (CNA-silica), this approach gave evidence for the following conclusions[2]: the main result of the amination by the CNA groups is a strong deactivation of the silica surface; the cyano groups are to a large extent (up to about 90% in *n*-hexane) adsorbed to the remaining silica sites; as a result, polycyclic aromatic hydrocarbons show skewed adsorption to the silica surface; the CNA layer stabilizes polar solute–adsorbent complexes; and the CNA groups show a small but significant specific interaction with (aromatic) nitrile and aldehyde groups.

This paper deals with the properties of Nucleosil 10 NH$_2$, a silica covered by aminobutylsilyl (ABS) groups. As the ABS group is a very strong Lewis base (electron donor), it can be expected that the ABS layer will considerably affect the acidic character of silica, and will show specific interactions with electron acceptor groups of the solute molecules.

THEORETICAL

The adsorption model of Snyder[3] and its application to monomeric bonded phases have been outlined in detail in previous papers[1,2,4]. It can be summarized with the following equations:

$$\log (V_N/W) = \log V_a + \alpha (S^0 - \varepsilon^0 A_s) \tag{1}$$

where V_N (cm^3) is the net retention volume, W (g) the weight of adsorbent in the column, α the adsorbent activity, S^0 is the solute Lewis base (or acid) strength, ε^0 the (mean) eluent strength and A_s the (effective) adsorbed surface area of the solute (expressed in units of 8.5 Å^2). V_a is the volume of a monolayer of adsorbed eluent per gram of adsorbent and can be estimated from

$$V_a = 35 \cdot 10^{-5} A - 0.01 \text{ wt.-}\% \text{ H}_2\text{O} \tag{2}$$

Therein, A (m^2/g) is the adsorbent specific surface area.

If steric effects are excluded, essentially four effects contribute to S^0. For disubstituted benzenes S^0 is given by the equation

$$S^0 = \sum_i Q_i^0 - \beta f(Q_k^0) Q_i^0 + \delta + \varrho_k \sigma_i \tag{3}$$

The term $\sum_i Q_i^0$ accounts for the adsorptive contributions of all solute groups i of the adsorbate. The second term on the right-hand side corrects for solute localization by the strongest adsorbed group k to the strongest sites of the energetically heterogeneous adsorbent surface. The third term, δ, is related to solute–eluent interactions, which become significant as the solute and/or eluent polarity increases. The term $\varrho_k \sigma_i$ describes the contribution of intramolecular electronic effects by a solute group i on the adsorptive strength of group k in terms of the well known Hammett σ constants[5]. As the values of Q_i^0 and those of the localization function $f(Q_k^0)$ were given by Snyder (on bare silica[3]), only the parameters β, σ and ϱ_k need to be determined. Their meaning will be related to the bonded phase properties under Results and Discussion.

The S^0 values of unsubstituted polycyclic aromatic hydrocarbons can be described by only two terms:

$$S^0 = n Q_{-C=}^0 - \zeta (n - 6) \tag{4}$$

The first term on the right-hand side is the sum of the contributions $Q_{-C=}^0$ of the n aromatic carbon atoms of the arenes, and the second term accounts for solute localization.

The term $-\alpha \varepsilon^0 A_s$ in eqn. 1 represents the primary eluent effect, which arises as a result of the replacement of adsorbed eluent by the adsorbate molecules. The A_s values of disubstituted benzenes are given by

$$A_s = \sum_i a_i \text{ (calc.)} + \gamma \sum_i \Delta a_i \text{ (SiO}_2\text{)} \tag{5}$$

where a_i (calc.) is the contribution of a non-localized solute group i to A_s, which can be calculated from Van der Waals radii and bond angles. The discrepancy between experimental and calculated a_s values, $\gamma \Delta a_i$ (SiO₂), observed for localized groups on bare silica, is accounted for by the last term in eqn. 5. The parameter γ appears to be related to the extent of deactivation of bare silica by water[6,7].

The A_s values of arenes on bare silica can be estimated from

$$A_s = 6 + 0.8 \, (h-6) + 0.25 \, (c-h) \tag{6}$$

where c and h are the numbers of carbon atoms and protons in the arenes, respectively.

The eluent strength (ε^0) data and the Q_i^0, $f(Q_k)$, a_i and Δa_i (SiO₂) values on bare silica collected by Snyder will also apply to bonded phases. Thus, any difference between the log V_N/W data on bare silica and on the bonded phase in question will be ascribed to different values of the parameters log V_a, α, β, γ, δ, ζ and ϱ_k.

The parameters α and log V_a are determined from a plot of log V_N/W data of monosubstituted benzenes in n-hexane ($\varepsilon^0 = 0$) against their S^0 values.

When α and log V_a are known, the S^0 values of the arenes can easily be obtained from their net retention data in n-hexane, and be plotted against n to give ζ according to eqn. 4.

As α and log V_a are independent of the eluent strength, A_s values can be calculated from

$$A_s = \frac{1}{\alpha \varepsilon_E^0} \cdot \log (V_{N,H}/V_{N,E}) \tag{7}$$

where $V_{N,H}$ and $V_{N,E}$ are the net retention volumes in n-hexane and an eluent E with strength ε_E^0. The value of γ is estimated from eqn. 5 using A_s values of mono-substituted benzenes.

Finally, β, δ and ϱ_k values are obtained from multiple regression analysis using the equation

$$\frac{1}{\alpha} \cdot \log [V_N(i-\varnothing-k)/V_N(\varnothing-k)] - (Q_i^0 - \varepsilon_E^0 a_i) = \delta - \beta f(Q_k^0) Q_i^0 + \varrho_k(E) \sigma_i \tag{8}$$

wherein $i-\varnothing-k$ represents a member of a solute series which has the strongest adsorbed group k in common. The value of a_i can be calculated from $a_i = a_i$ (calc.) $+ \gamma \varDelta a_i$ (SiO$_2$) according to eqn. 5. From the standard error of fit, it can be judged whether Hammett σ, σ^- or σ^+ constants[8] should be used in eqn. 8. The latter are appropriate if the electron-withdrawing or -repelling action of group i is favoured by mesomerism (*i.e.*, a resonance hydrid electron configuration involving the groups i and k).

EXPERIMENTAL

Chemicals and adsorbent characterization

All solutes (obtained from Fluka, Buchs, Switzerland) were of the highest available purity and were used as received. n-Hexane and dichloromethane were supplied by Baker (Deventer, The Netherlands) and were dried with molecular sieve 5A before use.

Nucleosil 10 NH$_2$ (Macherey, Nagel & Co., Düren, G.F.R.) was examined by the BET technique according to Broekhoff and Linsen[9]. Results for specific surface area, pore volume and pore diameter are given in Table I. Elemental analyses of Nucleosil 10 NH$_2$ showed the same C and N contents before and after treatment with 0.1 N hydrochloric acid. Mean results were 4.80 wt.-% C and 1.36 wt.-% N (with respect to bare silica), which corresponds to a surface concentration of 2.54 μmole/m^2 of aminobutylsilyl groups. The mean distance of adjacent ABS anchoring places is about 9.5 Å.

Apparatus and procedure

The column (precision-bore stainless steel, length 25 cm, I.D. 2.1 mm) was packed by the viscous-slurry packing method[10]. The slurry (15 wt.-% ABS-silica, particle diameter 10 μm, in n-butanol) was degassed and homogenized by ultrasonic treatment and forced into the column with n-hexane at 350 atm. Finally, 500 ml of dry dichloromethane was flushed through the column. The weight of adsorbent in the column was 0.43 g. The HETP of an unretained solute was about 0.15 mm at a linear flow-rate of 1 cm/sec using n-hexane as the eluent.

TABLE I

CHARACTERISTIC ADSORBENT PROPERTIES OF ODS-, CNA- AND ABS-SILICA

Property	ODS-silica	CNA-silica	ABS-silica
Monomer structure	$>$Si–(CH₂)₁₇CH₃ $\|$ OH	–N(CH₃) (CH₂)₂CN	$>$Si–(CH₂)₄NH₂ $\|$ OH
BET specific surface area (m²/g)	316 ± 2	263 ± 3	388 ± 2
Pore volume (ml/g)	0.60	1.05	1.44
Mean pore diameter (Å)	75	170	150
Surface concentration of monomers (μmole/m²)	1.64	1.25	2.54
Log V_a	−1.03 ± 0.04	−0.93 ± 0.05	−0.79 ± 0.04
α	0.50 ± 0.01	0.45 ± 0.01	0.39 ± 0.01
Fraction of adsorbed monomers (n-hexane)	0	0.88	0.95
$\Delta\varepsilon^0_{lc}$ (n-hexane)	0.00	0.04	0.09
$\Delta\varepsilon^0_{lc}$ (dichloromethane)	0.00	0.00	0.03

The apparatus and measuring technique have been described previously[1]. The solute sample size was smaller than 25 μg (UV detection at 254 nm). The reproducibility of triplicate V_N measurements was about 10 μl or 3 % for strongly adsorbed solutes. The adsorbent activity was monitored occasionally by measuring retention volumes of some polar solutes in n-hexane and appeared to be constant within experimental error during the whole measuring period.

The following eluents were used: n-hexane (H, $\varepsilon^0 = 0$), n-hexane–dichloromethane (65:35, v/v) (B, $\varepsilon^0 = 0.22$) and methylene chloride (C, $\varepsilon^0 = 0.32$). The eluent strength data were given by Snyder[6,7]. All measurements were made at 25°.

RESULTS AND DISCUSSION

Adsorbent activity

Experimental log (V_N/W) data for some monosubstituted benzenes and chlorobenzenes are given in Table II and are plotted against S^0 in Fig. 1. Contrary to the results on ODS- and CNA-silica, those on ABS-silica cannot be fitted accurately by eqn. 1. In order to establish which solutes behave anomalously, the log (V_N/W) data on ABS-silica are plotted against those on ODS-silica at 25° [1] in Fig. 2. The log (V_N/W) value of acetophenone at 25° on ODS-silica is not availble. It can be estimated from that at 43.5° by accounting for the effect of the slight difference of α at the two temperatures, which yields log $(V_N/W) = 2.13$. In Fig. 2, the data points 10 (methyl benzoate) and 11 (acetophenone) appear to deviate significantly from the straight line through the other data points. Regression analysis of the remaining log (V_N/W) data by eqn. 1 yields $\alpha = 0.39 \pm 0.01$ and log $V_a = -0.79 \pm 0.04$.

Compared with water-free bare wide-pore silica (where $\alpha = 0.83$; ref. 3) or ODS-silica (where $\alpha \approx 0.50$), the activity of ABS-silica is very small. The deactivation by the ABS groups is due to two effects. Firstly, the removal of reactive silanol groups by the silylation reaction reduces the value of α to about that of ODS-silica, where only free silanol groups are available for solute adsorption[1]. Secondly, the

TABLE II

LOG (V_N/W) DATA FOR MONOSUBSTITUTED BENZENES, CHLOROBENZENES, PHENOLS, ANILINES AND PYRIDINES IN n-HEXANE (H), n-HEXANE–DICHLOROMETHANE (65:35) (B) AND DICHLOROMETHANE (C) AT 25°

i	No.	i-Ø H	i-Ø B	i-Ø C	Isomer	i-ØCl H	i-ØOH B	i-ØOH C	i-ØNH$_2$ B	i-ØNH$_2$ C	i-C$_5$H$_5$N B	i-C$_5$H$_5$N C
H	1	-0.24	*	*		-0.22	1.63	0.96	0.76	-0.08	1.15	0.61
F	2	-0.25	*	*	m-		1.95	1.18	0.63	-0.25		
					p-		1.81	1.03	0.85	0.00		
Cl	3	-0.22	*	*	m-		2.01	1.22	0.63	-0.24		
					p-		1.93	1.14	0.75	-0.12	0.57	-0.07
Br	4	-0.19	*	*	m-		2.00	1.17	0.66	-0.24		
					p-		1.98	1.09	0.75	-0.14	0.57	-0.08
CH$_3$	5	-0.27	*	*	m-		1.57	0.73	0.73	-0.09		
					p-		1.57	0.74	0.83	0.03	1.30	0.74
SCH$_3$	6	0.32	*	*								
OCH$_3$	7	0.45	*	*	m-	0.38	1.92	0.94	1.01	0.03		
					p-		1.84	0.87	1.24	0.29		
NO$_2$	8	0.82	-0.33	*	m-	0.79	**	1.57	1.00	-0.13		
					p-		**	2.09	1.26	0.08		
CN	9	1.12	-0.17	-0.81	m-		**	1.51	1.14	-0.03	0.94	-0.06
					p-	1.07	**	1.82	1.21	0.02	1.01	0.06
CO$_2$CH$_3$	10	0.97	-0.20	-0.86	m-		**	1.26				
					p-		**	1.54				
COCH$_3$	11	1.38	0.07	-0.61	m-		**	1.52	1.45	0.26		
					p-		**	1.82	1.58	0.33		

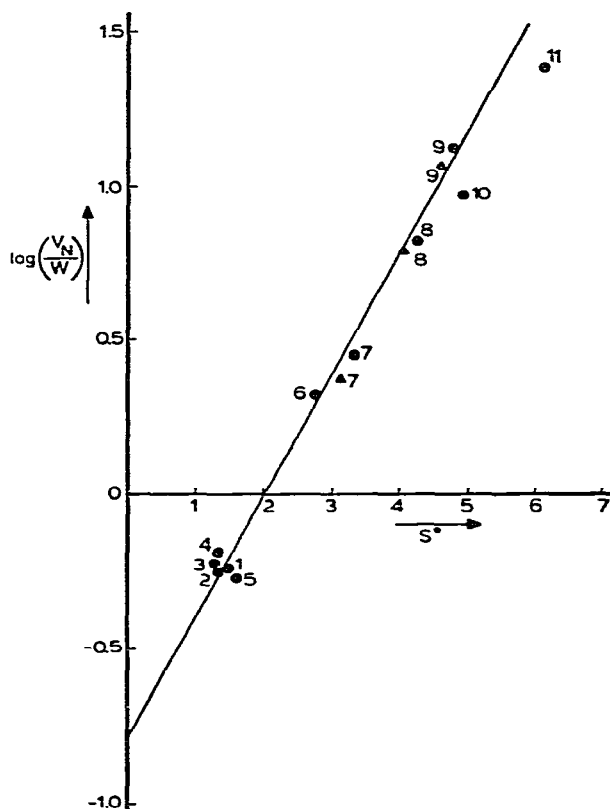* V_N values are very small.
** V_N values are very large.

Fig. 1. Experimental log (V_N/W) data for monosubstituted benzenes (●) and *m-* and *p-*substituted chlorobenzenes (▲) on ABS-silica *versus* S°. Eluent: *n*-hexane (25°). Numbering of the data points according to Table II.
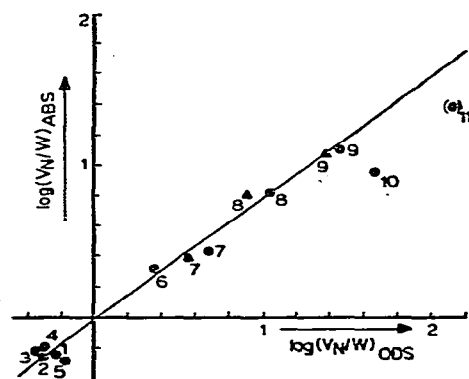
Fig. 2. Experimental log (V_N/W) data of monosubstituted (chloro)benzenes in *n*-hexane at 25° on ABS-silica *versus* those on ODS-silica. Numbering of the data points according to Table II.

adsorption of the ABS groups on the silica surface contributes to the eluent strength of *n*-hexane and reduces α further to its effective value of 0.39. Similar results have been obtained for CNA-silica. The fractions of adsorbed CNA and ABS groups and the effects on the eluent strength are given in Table I. The estimation of these data has been outlined previously[2]. In order to correct α and log V_a for ABS adsorption, the S^0 values must be adjusted by the term $-\varepsilon^0 A_s$. Here $\varepsilon^0 = 0.09$ (see Table I), whereas A_s is given by eqn. 5 using $\gamma = 0.61$ (value for ODS-silica). The corrected values are $\alpha = 0.47$ and log $V_a = -0.65$.

The estimated α value is close to that for ODS-silica ($\alpha = 0.50 \pm 0.01$). The log V_a value obtained, which holds for 1 g of silica plus bound monomers, must be corrected for the weight of the ABS layer before comparing it with theoretical estimates. This yields log $V_a = -0.59$. Eqn. 2 cannot be applied straightforwardly for the comparison because part of the silica surface is blocked by silyl groups (area about 25 Å²) and part of the ABS groups. Therefore, it can be expected that log $V_a \lesssim -1.07$, *i.e.* much smaller than the corrected experimental value of -0.59

(on ODS-silica this discrepancy is only about 0.08). This may be the result of interaction of ABS groups with the phenyl nucleus of the benzenes (discussed below).

Solute–ABS interaction

Although solute–silica interaction forces are of prime importance on ABS-silica, the retention behaviour of all solute types examined shows a definite change compared with that on ODS- and CNA-silica.

As mentioned above, methyl benzoate and acetophenone have relatively small S^0 values. In order to explain these anomalous values, attention will be focused first on the experimental S^0 values of the arenes presented in Table III. These values are plotted against the number of aromatic carbon atoms in Fig. 3.

TABLE III

LOG (V_N/W) DATA FOR SOME POLYCYCLIC AROMATIC COMPOUNDS IN n-HEXANE (H) AND n-HEXANE–DICHLOROMETHANE (65:35) (B) AT 25°, THEIR EXPERIMENTAL S^0 AND A_s VALUES AND CALCULATED A_s DATA

Solute	No.	H	B	S^0	A_s	A_s (calc.)
Benzene	1	−0.24	*	1.44		6.0
Naphthalene	2	0.21	*	2.58		8.1
Acenaphthene	3	0.31	*	2.85		9.7
Diphenyl	4	0.33	*	2.89		9.7
Fluorene	5	0.52	−0.73	3.38	14.6	9.9
Bibenzyl	6	0.38	*	3.02		12.4
Anthracene	7	0.66	−0.68	3.74	15.6	10.2
Phenanthrene	8	0.73	−0.59	3.92	15.4	10.2
Fluoranthene	9	0.94	−0.43	4.46	16.0	10.7
Chrysene	10	1.17	−0.29	5.04	17.0	12.3
Triphenylene	11	1.18	−0.31	5.08	17.4	12.3
p-Terphenyl	12	0.86	−0.79	4.24	19.2	13.4
3,4-Benzopyrene	13	1.31	−0.24	5.42	18.1	12.8
Perylene	14	1.41	−0.16	5.67	18.3	12.8
Picene	15	1.57	−0.10	6.07	19.5	14.4
Coronene	16	1.63	0.01	6.23	18.9	13.8
p,p'-Quaterphenyl	17	1.37	−0.52	5.57	22.0	17.1

* V_N values are very small.

In view of the localization of arenes, one might expect at first sight that their S^0 values would be close to those on ODS-silica. However, it must be taken into account that about 95% of the ABS groups are adsorbed silanol groups. Therefore, flat adsorption of the arenes can hardly be expected and accordingly the S^0 values should be similar to (or even smaller than) those on CNA-silica, where the same phenomenon occurs. Hence, the observed large S^0 values on ABS-silica (Fig. 3) indicate strong interaction forces between the arenes and free ABS groups. Further, the S^0 values of the fused arenes appear to be larger than those of the polyphenyls with the same number of aromatic carbon atoms. The data can be described by means of eqn. 4, using $Q^0_{-C=} = 0.25$ and $\zeta = -0.036 \pm 0.009$ (fused arenes) or $\zeta = 0.023 \pm 0.006$ (polyphenyls), although it is evident that these ζ values have no physical meaning. The data points 6 (bibenzyl) and 16 (coronene) in Fig. 3 have been excluded from this calculation. The relatively small S^0 value of coronene may be a
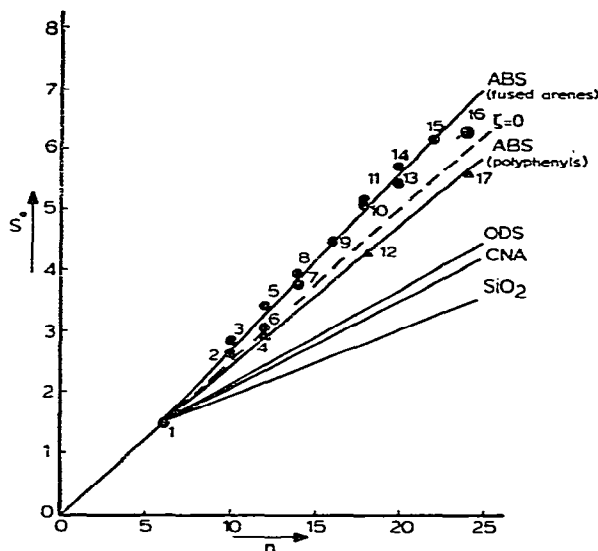
Fig. 3. Experimental $S°$ values of polycyclic aromatic hydrocarbons on ABS-silica in n-hexane (25°) *versus* the number of aromatic carbon atoms (n). Numbering of the data points according to Table III. Data points on bare silica, ODS- and CNA-silica have been omitted for the sake of clarity. Dashed line: expected on the basis of the additivity concept ($\zeta = 0$).

result of pronounced skewed adsorption as its diameter (9 Å) is about equal to the mean distance of adjacent monomer silyl groups. Bibenzyl behaves anomalously because it is not delocalized ($S° \approx 3.0$) on ABS- or ODS-silica or bare silica. Snyder[3,11] has suggested that the distance between both phenyl groups permits simultaneous adsorption of them on silanol sites*.

The discrepancy between the ζ values of the fused arenes and of the polyphenyl cannot be due to skewed adsorption of the slightly twisted polyphenyls[12] on the silica surface, because it is not observed on ODS- and CNA-silica. Further, neither the smallness of the ζ values nor their discrepancy on ABS-silica can be ascribed to dipole-induced dipole interaction, as the dipole of an ABS amino group is only one third of that of a CNA nitrile group and, moreover, the polarizabilities of benzenes, naphthalene and diphenyl[13] are linearly related to n. Therefore, it seems logical to assume that the arene–ABS interaction is of the donor–acceptor type and that its strength increases with the extent of π-conjugation in the arene. For equal numbers of aromatic carbon atoms the extent of π-conjugation is larger in a flat fused arene than in a slightly twisted polyphenyl. We presume that the adsorbed arenes are electron acceptors towards the ABS group which is a strong n-donor[14]. Complexes between arenes and electron acceptors have been examined extensively[15]. The work of Dewar and Thompson[16] on arene–tetracyanoethylene (TCNE) complexes in chloroform is noteworthy with respect to this work. The log K_c values (K_c, l/mole,

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* Previously, we expressed some doubt about this explanation because acenaphthene and fluorene also show relatively large $S°$ values (see Fig. 2 in ref. 1). However, this argument is not correct as the cycloalkyl moiety of the latter two solutes contributes to $S°$ to some extent (L. R. Snyder, personal communication), and this has not been accounted for. It is interesting that these solutes show "normal" behaviour on ABS-silica.

is the complex association constant) of some arene–TCNE complexes are plotted against n in Fig. 4. They show a similar pattern to that in Fig. 3. Presumably, on ABS-silica as well as in bulk solution and irrespective of the direction of charge transfer, the stability of the complex depends on the extent of π-conjugation in the arene. Hence we believe that on ABS-silica a "sandwich" complex of the type SiOH←arene←ABS may occur, but it need not be assumed to explain the results.
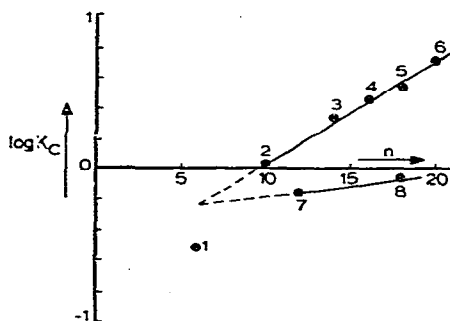

Fig. 4. Experimental log K_c values of some arene–tetracyanoethylene complexes in chloroform at 25°[16] *versus* the number of carbon atoms (n). 1 = Benzene; 2 = naphthalene; 3 = phenanthrene; 4 = pyrene; 5 = triphenylene; 6 = 3,4-benzpyrene; 7 = diphenyl; 8 = *p*-terphenyl.

The small S^0 values obtained for methyl benzoate and acetophenone can be explained similarly. The bulky methyl group forces the substituent group to turn slightly out of the plane of the phenyl ring on adsorption on the small crystalline flat surface regions of a wide-pore silica, and so disturb the π-conjugation between the substituent and the phenyl ring and weakens the interaction with the ABS group. The fact that "mesomeric interactions" occur on adsorption of the planar *p*-hydroxybenzaldehyde, but not with the non-planar *p*-hydroxyacetophenone, has been explained along the same lines[1,2]. ABS–phenyl interaction is probably also the cause of the large log V_a value mentioned above.

Primary eluent effects

Experimental log (V_N/W) data for some monosubstituted benzenes in the binary eluent (B) and in dichloromethane (C) are given in Table II. Data for the arenes in the binary eluent are presented in Table III. The use of $\alpha = 0.39$, $\varepsilon_B^0 = 0.22$ and $\varepsilon_C^0 = 0.32$ in eqn. 7 yields A_s values, from which γ_i values can be obtained[*].

The effective γ_i values of some monosubstituted benzenes in both eluents are given in Table IV. Previously, it has been shown that γ_i is independent of substituent i and of temperature[1,2]. Therefore, it is justifiable to compare the mean γ values of these bonded phases. On ODS- and CNA-silica the γ values are identical. Obviously, the solute and eluent molecules show approximately the same (and weak) interaction with ODS and CNA groups. So far, there is no reason to assume that γ depends on

* These γ_i values are about 0.07 too large in both eluents due to the contribution of the ABS groups to the eluent strength (and correspondingly to the α and log V_a values). This hardly significant effect will be omitted in the following discussion.

TABLE IV

γ_i VALUES FOR MONOSUBSTITUTED BENZENES ON ABS-SILICA IN n-HEXANE–DICHLOROMETHANE (65:35) (B) AND IN DICHLOROMETHANE (C) AND MEAN γ VALUES ON ABS-, ODS- AND CNA-SILICA

Adsorbent	Eluent	γ_i				$\bar{\gamma} \pm s_\gamma$
		NO_2	CN	CO_2CH_3	$COCH_3$	
ABS-silica	B	0.98	1.08	0.92	1.01	1.00 ± 0.07
	C		1.17	1.09	1.10	1.12 ± 0.04
ODS-silica	B					0.61 ± 0.05
CNA-silica	B					0.59 ± 0.03

the surface concentration of bound monomers (see Table I), provided that it is large enough to eliminate the reactive (or bound) silanol groups (0.5–1.0 μmole/m² on a wide-pore silica[2]) and small enough to guarantee flat adsorption of the benzenes. Therefore, it is assumed that the value of $\gamma \approx 0.60$ is characteristic for a silica surface covered merely by free silanol sites. From this point of view, the large γ values on ABS-silica should be ascribed to solute ABS interaction accompanied by the the breakdown of a relatively strong dichloromethane–ABS interaction. As the occurrence of weak donor–acceptor complexes of solvents such as chloroform and dichloromethane with amines cannot be ruled out[15], this explanation of the large γ values on ABS-silica seems plausible. The slight increase in γ with increasing dichloromethane concentration on ABS-silica is probably due to the increase in the mean number of dichloromethane molecules in the solvent shell around the ABS amino groups.

The experimental and calculated A_s values of the arenes are given in Table III and are plotted against each other in Fig. 5. The A_s values on ODS- and CNA-silica are also presented in Fig. 5 for the sake of comparison. On ODS-silica the A_s values
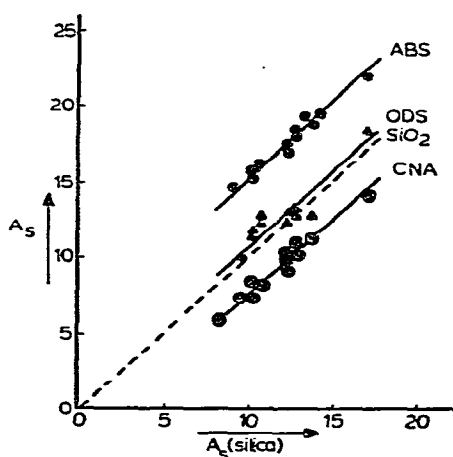

Fig. 5. Experimental A_s values of polycyclic aromatic hydrocarbons on ABS-, ODS- and CNA-silica *versus* calculated A_s (silica) values. Eluents: n-hexane and n-hexane–dichloromethane (65:35) at 25°.

are close to the calculated values, which hold for bare silica. This indicates flat adsorption on the silica surface beneath the ODS bristle layer. On CNS-silica the A_s values are about 2.5 smaller as a result of skewed adsorption, as mentioned above. The A_s values on ABS-silica are anomalously large. The mean discrepancy between the experimental and calculated values is 5.2 $\pm$ 0.1, although small A_s values would be expected in view of steric interference to flat adsorption by adsorbed ABS groups. Obviously, these steric effects are completely overruled by the competitive interaction of the arene and dichloromethane molecules with the ABS groups.

Adsorption behaviour of m- and p-substituted phenols, anilines and pyridines

Experimental log (V_N/W) values are given in Table II. An attempt to obtain retention data for substituted benzaldehydes failed, presumably because of a condensation reaction with the ABS group, catalysed by (acidic) silanol groups[17].

The phenols with strongly electron-withdrawing substituents could not be eluted with the binary eluent within reasonable time. As the remaining solutes of this series cover only small range of σ^- values, a three-parameter analysis will fail to give reliable results. Therefore, only retention data of the phenols in dichloromethane will be discussed below.

Multiple regression analyses of the data (left-hand side of eqn. 8) showed that the best fit can be achieved using σ^- and σ^+ substituent constants for the phenols and the pyridines, respectively. The data for the aniline series can be described equally well with σ or σ^- constants, because the influence of intramolecular effects on the adsorptive strength of these solutes appears to be small on ABS-silica. Optimal fit on applying σ^- or σ^+ constants indicates the possibility of direct "mesomeric interaction" between the substituent groups i and k on adsorption. Whether mesomerism causes anomalously large or small retention volumes depends on the sign of ϱ_k.

The values of β, ϱ, σ and the standard error of fit (s) in the binary eluent and n dichloromethane are given in Table V.

TABLE V

VALUES OF β, ϱ, δ AND THE STANDARD ERROR OF FIT (s) FOR m- AND p-MONO-SUBSTITUTED PHENOLS, ANILINES AND PYRIDINES IN n-HEXANE–DICHLORO-METHANE (65:35) (B) AND DICHLOROMETHANE (C) AT 25°

Solute series		Parameter	B	C
Phenols	(σ^-)	$\beta \pm s_\beta$		0.56 $\pm$ 0.10
Anilines	(σ)		0.34 $\pm$ 0.15	0.20 $\pm$ 0.10
Pyridines	(σ^+)		0.22 $\pm$ 0.14	0.10 $\pm$ 0.20
Phenols	(σ^-)	$\varrho \pm s_\varrho$		2.56 $\pm$ 0.20
Anilines	(σ)		−0.24 $\pm$ 0.24	−0.46 $\pm$ 0.26
Pyridines	(σ^+)		−2.19 $\pm$ 0.31	−2.42 $\pm$ 0.45
Phenols	(σ^-)	$\delta \pm s_\delta$		0.25 $\pm$ 0.09
Anilines	(σ)		0.25 $\pm$ 0.09	0.32 $\pm$ 0.10
Pyridines	(σ^+)		−0.26 $\pm$ 0.12	−0.30 $\pm$ 0.18
Phenols	(σ^-)	s		0.26
Anilines	(σ)		0.25	0.27
Pyridines	(σ^+)		0.19	0.28

The influence of the eluent strength on β, ϱ and σ appears not to be significant on either ABS- or CNA-silica[2]. On ODS-silica, however, ϱ increases significantly with increasing eluent strength[1]. Obviously, the (polar) solute–adsorbent complexes are better stabilized in polar solvents. This stabilization is surprisingly well fulfilled by the CNA and ABS monomers, as their contribution to the strength of the binary eluent is only about 0.02 and 0.05, respectively.

The mean β and ϱ values on the three bonded phases will be discussed on the basis of the solute–adsorbent structures I, II and III presented in Fig. 6.

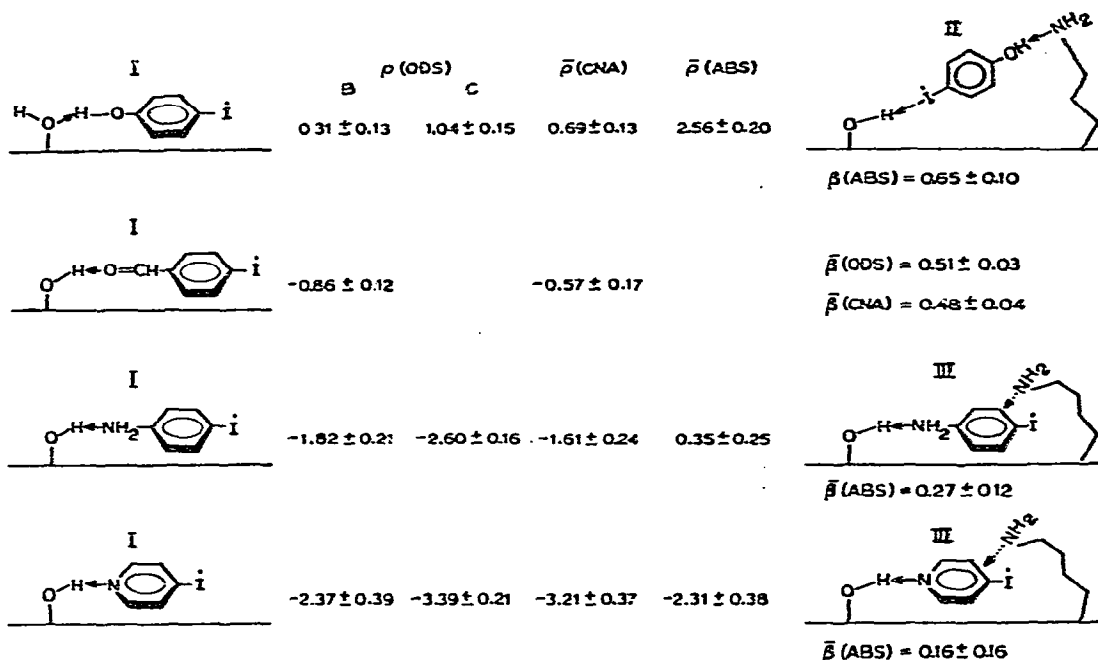Fig. 6. Experimental ϱ and β values of m- and p-substituted phenols, benzaldehydes, anilines and pyridines on ODS- (eluents B and C), CNA- and ABS-silica (mean ϱ values in eluents B and C), and the corresponding structures of the solute–adsorbent complexes on ODS- and CNA-silica (I) and on ABS-silica (phenols, I and II; anilines and pyridines, I and III).

The ϱ values on ABS-silica are considerably more positive than those on ODS- and CNA-silica, particularly in dichloromethane. Obviously, the ABS groups are involved in the adsorption process.

For the phenols, it can be assumed that the acidic OH group forms a strong hydrogen bond with the ABS group. The transferred charge from the ABS group can be withdrawn by group i and may even be transmitted to an available (acidic) silanol site (structure II). As σ_i (or σ_i^-) is a measure of the electron-withdrawing ability of group i, it can be expected that the occurrence of the complex II will contribute to the ϱ value. On ODS-silica, and presumably also on CNA-silica, merely the structure I occurs, as will be elucidated below by means of the β values on these adsorbents.

The basic anilines and pyridines will preferably form a hydrogen bond with the silanol groups on all three adsorbents. In addition, the ABS group can form a

donor–acceptor complex with the group i (or the $\varnothing$–i moiety) of these solutes (III). The associated charge transfer opposes electron withdrawal by group i and hence ϱ will shift to less negative values on ABS-silica.

The mean β values on ODS- and CNA-silica are identical within experimental error[1,2]. According to the adsorption model of Snyder, β decreases with increasing number of accessible active sites per square metre. Therefore, solute–CNA interactions, if present, are of minor importance. Obviously, the value $\beta \approx 0.50$ accounts for solute localization on a water-free silica surface covered merely by active free silanol sites.

The small β values of the anilines and pyridines indicate an increased solute localization. These molecules are adsorbed flatly on a silanol site (I) and in addition can be subject to interactions exerted by the flexible ABS sites (III).

The β value of the phenols on ABS-silica is relatively large. Probably, hydrogen bonding to the flexible ABS site is accompanied by an unfavourable position of the i–$\varnothing$ moiety to the silica surface (II). Thus, localization to the ABS group can imply delocalization of the i–$\varnothing$ group and hence an increased β value.

CONCLUSIONS

The adsorption theory of Snyder appears to be a valuable means of evaluating the adsorptive properties of Nucleosil 10 NH_2.

The effective activity of this bonded phase is small ($\alpha = 0.39$) compared with that of bare wide-pore silica ($\alpha \approx 0.83$) and ODS-silica ($\alpha = 0.50$). This is a result of preferential deactivation of reactive silanol groups and a considerable contribution of the ABS groups to the eluent strength of n-hexane.

The contribution of solute–ABS interactions can be explained in terms of donor–acceptor complexation (including hydrogen bonding).

These donor–acceptor interactions give rise to the large S^0 values of the fused arenes. Their contribution appears to depend on the extent of π-conjugation. The experimental S^0 values obtained for polyphenyls, methyl benzoate and acetophenone are accordingly relatively small: the benzenes mentioned cannot be adsorbed flatly on the silica surface, whereas the twisted polyphenyls experience strain on flat adsorption, which restricts π-conjugation.

The anomalously large contribution of eluent localization to the A_s values of the arenes and the monosubstituted benzenes [γ (binary eluent) $= 1.00$ and γ (dichloromethane) $= 1.12$] is the result of competitive solute–ABS and dichloromethane–ABS interactions.

The ϱ values of m- and p-substituted phenols are more positive and those of the anilines and pyridines are less negative than the values obtained on ODS- and CNA-silica. This shift of the ϱ values indicates hydrogen bonding between the phenolic OH and a free ABS group and to interaction of an ABS group with the electrophilic parts of the aniline and pyridine molecules. Owing to the very effective stabilization of the polar solute–adsorbent complexes by the ABS groups, the ϱ values are not significantly affected by an increase of the eluent strength. The solute localization parameters β are larger (phenols) and smaller (anilines and pyridines) than those on ODS- and CNA-silica ($\beta = 0.50$), where only free silanol sites are involved in adsorption.

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