Journal of Chromatography, 168 (1979) 9–25

CHROM. 11,344

ADSORPTIVE PROPERTIES OF N-2-CYANOETHYL-N-METHYLAMINOSILICA IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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(Received June 20th, 1978)

SUMMARY

Net retention volumes per gram of N-2-cyanoethyl-N-methylaminosilica have been measured for a large number of mono- and disubstituted benzenes, some monosubstituted (cyclo)hexanes and a number of unsubstituted polycyclic aromatic hydrocarbons, using *n*-hexane, methylene chloride and a mixture of both solvents as eluent at 25° and 43.5°.

The retention data are interpreted in terms of the semi-empirical adsorption model, developed by Snyder for bare adsorbents. The effects of adsorbent deactivation (due to the amination and the adsorption of the cyano group to the silica), temperature, solute and eluent localization, change of charge distribution in the solute molecule by substituents and mode of adsorption of the solute on retention are discussed.

INTRODUCTION

Chemically modified silicas are well known adsorbents in high-performance liquid chromatography (HPLC). As far as the structure of the bound organic layer is concerned, two types can be distinguished. In the first type of adsorbent the bound layer has a network structure as a result of the polymerization of the monomers on the silica surface. The second type of adsorbent has a thin layer of non-polymerized monomers.

In previous papers, the adsorptive properties of octadecylsilyl-(ODS)-silica, an apolar adsorbent of the second type, have been discussed[1,2] in terms of the adsorption model of Snyder[3]. It has been shown that this theory gives a good description of the experimental retention data of substituted benzenes and (cyclo)hexanes and of polycyclic aromatic hydrocarbons in the eluents *n*-hexane, methylene chloride and in a mixture of these solvents. As a result of the deactivation of the silica by the ODS monomers, the parameters in Snyder's model had to be adjusted.

In this paper, the results obtained on a polar monomeric bonded phase, N-2-cyanoethyl-N-methylaminosilica (CNA-silica), are discussed and compared with those on ODS-silica.

THEORETICAL

The adsorption theory of Snyder[3] has been reviewed briefly in previous papers[1,2]. Therefore, we present here only the basic equations and elucidate the procedure of the estimation of the parameters of the model.

The net retention volume of a solute per gram silica is given by the equation[3]

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

where

$$V_a = 3.5 \cdot 10^{-4} A - 0.01 \text{ wt.-\% } H_2O \tag{2}$$

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

$$A_s = \sum_i a_i \text{ (calc.)} + \gamma \sum_i \Delta a_i \text{ } (SiO_2) \tag{4}$$

W (g) is the weight of adsorbent in the column. V_a is the volume of a monolayer of adsorbed eluent per gram adsorbent. It can be estimated for bare adsorbents by eqn. 2 if the specific surface area of the adsorbent, A (m^2/g), and the amount of adsorbed water are known. For a water-free (standard) adsorbent, the adsorbent activity $\alpha = 1$ (arbitrary value).

Porous silica particles have an energetically heterogeneous adsorbent surface. The strongest adsorption sites are the hydrogen-bond-linked (reactive) silanol groups. Water adsorbs preferentially at these acidic sites, and as a result α decreases sharply. Further addition of water gradually covers the less active free silanol groups and α steadily decreases to a value of about 0.7 (wide-pore silica)[3]. For wide-pore silicas it can be estimated from the graph of α *versus* the weight-percent of adsorbed water[3] that about 15% of all silanol groups are of the reactive type. As these silicas have about 8 μmole/m^2 of silanol groups[4], only 1 μmole/m^2 of reactive silanol groups is present. This conclusion is in accord with that of Snyder and Ward[5], who estimated a coverage of 5% of reactive silanol groups (0.5 μmole/m^2), and is of crucial importance for the understanding of the adsorptive properties of chemically modified silicas.

The third type of sites, the siloxane groups, have small (if any) activity towards polar and unsaturated adsorbate molecules[3] and can be left out of consideration for liquid–solid adsorption equilibria. S^0 and ε^0 are measures of the Lewis base (or acid) strength of the solute and the eluent, respectively. For alkanes $\varepsilon^0 = 0$ (arbitrary value). Hence, S^0 can be determined on a standard adsorbent from eqn. 1, if A is known and *n*-hexane is used as the eluent. Conversely, α values can be obtained for any adsorbent from experimental $\log(V_N/W)$ data for a series of solutes, if their S^0 values on silica are known. In the following, only adsorbate molecules that show flat adsorption on to silica (unless stated otherwise) and wherein steric crowding of solute groups can be excluded are considered. The S^0 values are composed of essentially three contributions. The term $\sum_i Q_i^0$ in eqn. 3 represents the sum of the Q_i^0 values of the group i of the adsorbate. However, this additivity concept has limited validity. It implies that all solute groups i can be adsorbed on to silanol sites and that the adsorptive strength of any solute group is independent of all other groups in the adsorbate

molecule. Both statements are false, however, and the required corrections are accounted for by the last two terms in eqn. 3.

As the mean mutual distance of the silanol groups is about 5 Å (ref. 4), it is evident that the positions of substituents in the solute molecule generally do not match those of the silanol sites on the adsorbent. Suppose group k is the strongest adsorbing group ($Q_k^0 > Q_{i\neq k}^0$). The group k will preferably be localized on to a site, whereas all other groups will be more or less delocalized, *i.e.*, show less strong adsorption than would be possible in a localized position. This difficult problem can only be solved by fixing the Q_i^0 values for two standard series of solutes (*i.e.*, monosubstituted benzenes and alkanes), the adsorptive strength of which is given by $S^0 \equiv \sum_i Q_i^0$. These two sets of Q_i^0 values are given in Table I. Snyder has shown that the correction for delocalization is proportional to $\sum_{i\neq k} Q_i^0$, to the extent of localization of group k [denoted by the factor $f(Q_k^0)$] and to a parameter β, which accounts for the "action radius" of a particular type of sites ($\beta = 1$ for alumina, $\beta < 1$ for the more accessible and revolving silanol groups). Empirical values of $f(Q_k^0)$ for substituted benzenes on alumina (given in Table I) have also been applied to ODS-silica[2]. Obviously, solute localization is complete if $Q_k^0 \gtrsim 4$.

The second correction term in eqn. 3 accounts for intramolecular electronic effects on the adsorptive strength of group k by other solute groups. As the solute–adsorbent interaction forces are of the Lewis acid–base type[6], these effects can be described by means of Hammett σ_i constants[7]. Suppose, we are dealing with a series of i-substituted phenols. The electron-withdrawing (or -repelling) action of group i increases (or diminishes) the acid strength of the phenolic hydroxyl group and increases (or decreases) S^0 accordingly. The parameter ϱ_k is characteristic of group k (hydroxyl group of phenols), but it also depends on the solvent polarity and slightly on temperature. It is a measure for the susceptibility of group k for intramolecular charge shifts induced by group i. As $\sigma_i > 0$ for electron-withdrawing substituents, ϱ_k will be positive or negative, respectively, when group k is a proton donor or a proton acceptor. respectively, towards the adsorbent sites. The parameter δ has been introduced previously[2] to improve the fit of experimental $\log(V_N/W)$ data to eqn. 1. Its physical meaning is obscure, but probably it is connected with solute–eluent interaction contributions, which may be significant for very polar solutes such as phenols.

It is well known that solute retention decreases with increasing eluent strength (ε^0). According to eqn. 1, this decrease is proportional to A_s. To a first approximation, $A_s = \sum_i a_i(\text{calc.})$, where $a_i(\text{calc.})$ is the area of the solute group i, normalized to that of benzene (51 Å$^2 \triangleq A_s = 6$). $S^0(\text{benzene}) = 6\ Q^0_{-C=} = 1.5$. It is evident from eqn. 1 that $S^0 - \varepsilon^0 A_s = 0$ if benzene is eluted with benzene. Hence $\varepsilon^0(\text{benzene}) = 0.25$. However, as benzene is not localized, this ε^0 value, and all other ε^0 values derived in the same way, represent solvent strengths towards an energetically homogeneous adsorbent. In consequence, the ε^0 values represent an average adsorptive strength of all eluent molecules in the adsorbed monolayer. Hence, a localized solute group i has to desorb eluent molecules, which are more strongly adsorbed than corresponds to the ε^0 value of this eluent. This explains why the experimental a_i values of localized groups are larger than $a_i(\text{calc.})$. This discrepancy has been accounted for by the term $\gamma \sum_i \Delta a_i(SiO_2)$ in eqn. 4. The $\Delta a_i(SiO_2)$ values can be calculated from the difference in $a_i(\text{exp.})$ and $a_i(\text{calc.})$ data given in Table I and appear to increase with increasing $f(Q_i^0)$ values, as expected. The

TABLE I

Q_i^0, $f(Q^0)$, σ_i, CALCULATED AND EXPERIMENTAL a_i VALUES OF SUBSTITUENT GROUPS i AT A PHENYL NUCLEUS, AND Q_i^0 AND a_i VALUES OF GROUPS IN AN ALIPHATIC COMPOUND

i	$Q_i^0(Ø-)$ *	$f(Q_i^0)$ **	σ_i ***	$a_i(calc.)$ *	$a_i(exp.)$ *	$Q_i^0(R-)$ *	$a_i(calc.)$ *	$a_i(exp.)$ *
CH_3	0.11	0	m −0.07 p −0.17	0.8	0.8	0.07	1.6	1.6
CH_2	0.07	0		0.9	0.9	−0.05	0.9	0.9
CH=	0.25	0		1.5	1.5	0.25		
F	−0.15	0	m 0.34 p 0.06	0.4	0.4	1.54	1.2	1.2
Cl	−0.20	0	m 0.37 p 0.23	0.7	0.7	1.74	1.5	1.2
Br	−0.17	0	m 0.39 p 0.23	1.0	1.0	1.94	1.8	1.8
SH	0.67	0	m 0.25 p 0.15	0.9	0.9	1.70	1.8	3.3
SCH_3	1.29	0.02	m 0.15 p 0.00	1.7	3.2	2.94	2.6	7.4
OCH_3	1.83	0.13	m 0.12 p −0.27	1.1	4.6	3.61	2.1	9.0
NO_2	2.77	0.30	m 0.71 p 0.78	1.3	7.5	5.71	2.3	9.5
CN	3.33	0.40	m 0.56 p 0.66	0.6	8.4	5.27	1.5	8.7
CHO	3.48	0.42	m 0.36 § p 0.43 §	1.1	8.3	4.97	2.0	9.2
CO_2CH_3	3.45	0.42	m 0.37 p 0.45	2.3	8.1	5.27	3.2	10.5
$COCH_3$	4.69	0.45	m 0.38 p 0.50	1.5	9.2	5.27	2.6	9.8
OH	4.20	0.45	m 0.12 p −0.37	0.4	7.6	5.60	1.3	8.5
NH_2	5.1	0.45	m −0.16 p −0.66	0.6	8.7	8.0	1.5	8.7
Pyridyl	6.1 §§	0.45						

* Experimental data given by Snyder[3].
** Interpolated data from smoothed values[3].
*** Data given by Ritchie and Sager[8].
§ Data given by Humffray *et al.*[9].
§§ Experimental value given by Snyder[10].

parameter γ needs some further comment. For a narrow-pore silica, Snyder[11,12] found $\gamma = 0$ (water-free adsorbent) and $\gamma = 1$ (16 wt.-% of adsorbed water). Obviously, eluent localization is important only when the reactive silanol groups are (largely) deactivated by adsorbed water and only free silanol groups are left on the silica surface. The predominant role of active single silanol groups on eluent localization is also evident on water-free ODS-silica, where $\gamma = 0.61$ due to the elimination of the reactive silanol groups by the silylation reaction[2].

It has been shown previously[2] that γ should be determined first, from experimental A_s values for monosubstituted benzenes. Then, if γ_i is independent of Q_i^0 and ε^0 (*i.e.*, according to the model), the parameters β, δ and ϱ_k can be obtained from experi-

mental $\log(V_N/W)$ data for a series of *m*- and *p*-disubstituted benzenes, which have group *k* in common:

$$\frac{1}{\alpha} \cdot \log[V_N(i\text{Ø}k)/V_N(\text{Ø}k)] - (Q_i^0 - \varepsilon^0 a_i) = \delta - \beta f(Q_k^0)Q_i^0 + \varrho_k \sigma_i \quad (5)$$

Values of β, δ and ϱ_k are found by applying multiple regression analysis to the data calculated for the left-hand side of eqn. 5.

In the foregoing, attention has been focused on substituted benzenes. The S^0 values of unsubstituted polycyclic aromatic hydrocarbons on silica can be estimated from the equation[3]

$$S^0 = \frac{1}{\alpha} \cdot \log(V_N/WV_a) = nQ^0_{-C=} - \beta f(Q_k^0)\,(n-6)Q^0_{-C=} \equiv nQ^0_{-C=} - \zeta(n-6) \quad (6)$$

wherein *n* is the number of aromatic carbon atoms and ζ is a delocalization parameter. On narrow-pore silica $\zeta = 0.11$, whereas $\zeta = 0.14$ for a wide-pore silica[13]. Snyder[12] has related the smaller extent of delocalization on narrow-pore silica to the preferential adsorption of unsubstituted polyaromatic compounds to clusters of reactive silanol groups, which are abundantly present on its irregular surface. On (wide-pore) ODS-silica $\zeta = 0.095$ (ref. 2). Hence, ζ seems to increase with increasing adsorbent heterogeneity.

Eqn. 6 also affords the possibility of judging whether adsorbate molecules adsorb flatly on to a chemically modified silica surface. A negative deviation from the calculated S^0 value (eqn. 6) is to be expected if the mean diameter of the adsorbate molecule is larger than the mean mutual distance of adjacent monomers.

The A_s values of polycyclic aromatics are given by the empirical equation[3]

$$A_s = 6 + 0.8(h - 6) + 0.25(c - h) \quad (7)$$

wherein *h* and *c* are the numbers of protons and carbon atoms of the adsorbate molecule, respectively. Solutes which show anomalously small S^0 values, due to steric hindrance of adsorption by the bonded phase monomers, will also show relatively small A_s values.

It can be expected from eqn. 1 that in polar eluents the alkyl moiety of monosubstituted (cyclo)hexanes will not be adsorbed completely. The number of adsorbed methylene groups (*m*) of these molecules can be calculated from the equation

$$A_s = a_i(\text{calc.}) + \gamma \Delta a_i(SiO_2) + m\, a_{CH_2} \quad (8)$$

Comparison of the magnitude of *m* on bare and modified silica gives an indication for steric shielding of the silica surface by the bound monomers.

EXPERIMENTAL

Chemicals

All solutes (obtained from Fluka, Buchs, Switzerland) were of the highest available purity and were used as received. The solvents *n*-hexane and methylene chloride were supplied by Baker (Deventer, The Netherlands) and dried on molecular sieve 5A overnight before use.

Preparation of N-2-cyanoethyl-N-methylaminosilica[14]

A 6-g amount of Merckosorb Si 100 (E. Merck, Darmstadt, G.F.R.) with an average particle size of about 10 μm was refluxed with 2 *N* hydrochloric acid for 2 h. The activated adsorbent was washed until chloride-free and dried at 150° and 1 mmHg for 12 h in a three-necked flask. The adsorbent was covered with a cooler, a dropping funnel and an inlet to bubble dry nitrogen through the silica suspension. The chlorination reagent [5 ml of freshly distilled[15] thionyl chloride (Fluka) in 20 ml of dry *n*-pentane] was added dropwise while the flask was gently swirled. The reaction mixture was allowed to reflux for 5 h. The chlorinated silica was rinsed carefully with dry diethyl ether by decantation, and finally covered with 50 ml of diethyl ether. A solution of 5 g of N-2-cyanoethyl-N-methylamine (CNA, Fluka) in 20 ml of dry diethyl ether was added dropwise. The reaction mixture was allowed to reflux for 6 h and kept under nitrogen at room temperature overnight. The product was rinsed with ethanol, 50% aqueous ethanol, acetone and diethyl ether, and dried at 100° and 1 mmHg for 2 h.

Adsorbent characterization

The BET technique after Broekhoff and Linsen[16] applied to Merckosorb Si 100 gave values of 263 $\pm$ 3 m^2/g for the specific surface area, 1.05 ml/g for the pore volume and 170 Å for the mean pore diameter. The corresponding values given by the supplier are 400 m^2/g, 1.00 ml/g and 100 Å. A similar discrepancy between our BET data on Merckosorb Si 60 and those given by Merck has been reported previously[2]. As our BET surface area of Partisil 10 (399 $\pm$ 2 m^2/g) is in agreement with that given by Reeve Angel (Clifton, N.J., U.S.A.) (400 m^2/g), the specifications of Merck have been rejected.

The results of the elemental (C, N) analysis yields a surface concentration of 1.25 μmole/m^2 of CNA monomers. The mean distance between adjacent CNA groups, estimated from this value, was about 13 Å.

Apparatus and procedure

The apparatus was a Packard-Becker (Delft, The Netherlands) Model 8200 chromatograph equipped with a UV and a refractive index detector. The eluent flow-rate was monitored continuously with a calibrated siphon counter (Waters Assoc., Milford, Mass., U.S.A.). The column (precision-bore stainless steel, length 25 cm, I.D. 2.1 mm) was packed by forcing a de-gassed and homogenized slurry (8 wt.-% CNA-silica in tetrachloromethane) into the column with *n*-hexane at 350 atm. Finally, 200 ml of *n*-hexane, absolute methanol and dry methylene chloride were flushed through the column. The weight of CNA-silica in the column was 0.38 g. The HETP of an unretained solute was about 0.2 mm at a linear flow-rate of 1 cm/sec using *n*-hexane as eluent.

The solute sample size was about 20 μg, except for polar (cyclo)hexane derivatives, to be detected by the refractive index detector (100 μg). The influence of the sample size appeared to be small: a sample of 0.2 μg of *p*-nitroanisole has a retention volume that is only 2% larger that of a 20-μg sample. Retention volumes were corrected for eluent hold-up in the column and dead volumes by means of the retention of *n*-pentane. All measurements were made at least in triplicate. The reproducibility of the retention volume is about 8 μl, except for strongly adsorbing solutes, for which

it is about 2%. The following eluents were used: *n*-hexane (H, $\varepsilon^0 = 0.0$), *n*-hexane–methylene chloride (65:35) (B, $\varepsilon^0 = 0.22$) and methylene chloride (C, $\varepsilon^0 = 0.32$). The ε^0 value of methylene chloride was given by Snyder[12], whereas that of the binary eluent was obtained by interpolation of experimental data of a series of *n*-pentane–methylene chloride mixtures[12].

RESULTS AND DISCUSSION

Adsorbent activity

Experimental $\log(V_N/W)$ data for monosubstituted benzenes and chlorobenzenes are given in Table II. S^0 values were calculated from the Q_i^0 values given in Table I. The $\log(V_N/W)$ data for both solute series can be described by eqn. 1 with α and $\log V_a$ values which are equal within experimental error. Therefore, both series can be combined and give

$$\text{at } 25^\circ : \alpha = 0.44 \pm 0.01, \log V_a = -0.91 \pm 0.04$$

$$\text{at } 43.5^\circ: \alpha = 0.46 \pm 0.01, \log V_a = -0.94 \pm 0.04$$

TABLE II

LOG(V_N/W) DATA FOR MONOSUBSTITUTED (CHLORO)BENZENES IN *n*-HEXANE (H, $\varepsilon^\circ = 0.0$) AND *n*-HEXANE–METHYLENE CHLORIDE (65:35) (B, $\varepsilon^\circ = 0.22$) AT 25° AND 43.5°

i	*No.*	Ø			*Cl-Ø*		Ø			*Cl-Ø*	
		H, 25°	*B, 25°*		*H, 25°*	*B, 25°*	*H, 43.5°*	*B, 43.5°*		*H, 43.5°*	*B, 43.5°*
H	1	−0.26	−*		−0.37	−*	−0.24	−*		−0.34	−*
											−*
F	2	−0.37	−*	*m*	−0.36	−*	−0.28	−*	*m*	−0.43	−*
				p	−0.38	−*			*p*	−0.40	−*
Cl	3	−0.37	−*	*m*	−0.36	−*	−0.34	−*	*m*	−0.50	−*
				p	−0.39	−*			*p*	−0.52	−*
Br	4	−0.37	−*	*m*	−0.34	−*	−0.25	−*	*m*	−0.48	−*
				p	−0.37	−*			*p*	−0.48	−*
CH_3	5	−0.13	−*	*m*	−0.36	−*	−0.20	−*	*m*	−0.35	−*
				p	−0.33	−*			*p*	−0.33	−*
SCH_3	6	0.24	−0.55				0.33	−0.54			
OCH_3	7	0.54	−0.33	*m*	0.34	−0.47	0.67	−0.37	*m*	0.40	−0.66
				p	0.42	−0.38			*p*	0.51	−0.52
NO_2	8	0.85	−0.17	*m*	0.70	−0.26	0.92	−0.15	*m*	0.77	−0.33
				p	0.71	−0.23			*p*	0.80	−0.25
CN	9	1.34	0.14	*m*	1.21	0.03	1.36	0.18	*m*	1.29	0.09
				p	1.28	0.13			*p*	1.37	0.15
CHO	10	1.40	0.33	*m*	1.22	0.16	1.52	0.42	*m*	1.29	0.19
				p	1.35	0.27			*p*	1.44	0.29
CO_2CH_3	11	1.25	0.19				1.40	0.24			
$COCH_3$	12	1.79	0.55				1.86	0.61			
				p	1.70	0.49			*p*	1.77	0.53

* V_N values are very small.

A typical plot of $\log(V_N/W)$ *versus* S^0 is presented in Fig. 1. The data points 8 (nitrobenzenes), 9 (benzonitriles) and 10 (benzaldehydes) deviate significantly from the line. The average deviations, ΔS^0, are 0.29 $\pm$ 0.06 (nitro group), -0.31 ± 0.10 (cyano group) and -0.30 ± 0.15 (aldehyde group), whereas the other solute points show a mean absolute deviation from the line of 0.04. A similar ΔS^0 value for the nitro group (0.25 ± 0.05) has been obtained on ODS-silica[2]. It is difficult to decide whether this deviation is due to the deactivation of the silica or to the inaccuracy of the Q_i^0 value of the nitro group. The ΔS^0 values of the cyano and the aldehyde groups seem to be typical for CNA-silica. Omission of the deviating data points leaves the α and $\log V_a$ values unchanged.

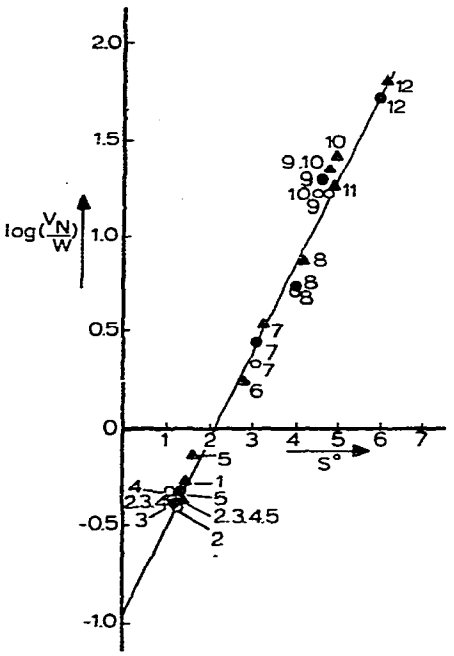

Fig. 1. Experimental $\log(V_N/W)$ data for monosubstituted benzenes (▲) and *m*- (○) and *p*-substituted chlorobenzenes (●) on CNA-silica *versus* S^0. Eluent: *n*-hexane (25°). Numbering of the data points according to Table II.

The influence of temperature on α and $\log V_a$ is very small. Hence, the adsorption process is controlled by enthalpic interaction forces. The small value of α is due to the elimination of the reactive silanol groups by the CNA monomers. As discussed in the theoretical section, a comparable wide-pore silica such as Davison Code 62 ($\alpha \approx 0.83$)[3], has a surface concentration of 0.5–1 μmole/m^2 of reactive silanol groups. As the CNA surface concentration is 1.25 μmole/m^2, it can be expected that on CNA-silica only free silanol sites are present, *i.e.*, that the silica surface beneath the CNA bristles is energetically homogeneous. The same holds for the ODS-silica (1.64 μmole/m^2 of ODS) examined previously. Nevertheless, the α value of CNA-silica is smaller than that of ODS-silica (0.51 ± 0.01). It can be expected that the cyano groups of the

bonded phase adsorb on to free silanol groups. However, this would affect α only if the siloxane groups contribute to the adsorbent activity, and there is little evidence for this assumption[17]. Therefore, we suppose that the flexible CNA monomers increase the eluent strength of *n*-hexane near the silica surface, owing to the adsorption of the polar cyano group. As a result, V_N decreases and a lower effective value of α is found. The plausibility of this explanation has been examined in the Appendix. It suffices here to note that on Nucleosil-NH_2 covered with 2.54 μmole/m^2 of very strongly adsorbing aminobutyl groups, a correspondingly larger decrease in α to 0.39 has been observed[18]. Obviously, polar groups connected to the silica surface by a flexible alkyl chain increase the eluent strength near the silica surface so that a lower effective adsorbent activity is found. As it is difficult to predict the true value of α quantitatively on a firm theoretical basis, the effective α and $\log V_a$ values given above are considered to be typical for the present CNA-silica and are used in further calculations.

Eluent localization

The magnitude of γ was estimated from $\log(V_N/W)$ data for monosubstituted benzenes in *n*-hexane and the binary eluent, as outlined in the theoretical section. The results are given in Table III, together with the results of a variance analysis. The *F*-

TABLE III

γ VALUES OF MONOSUBSTITUTED BENZENES AND THE RESULTS OF THE VARIANCE ANALYSES

Temperature (°C)	$\gamma_{i,T}$					$\bar{\gamma}_T \pm s_{\gamma_T}$
	$i = NO_2$	$i = CN$	$i = CHO$	$i = CO_2CH_3$	$i = COCH_3$	
25	0.51	0.74	0.60	0.46	0.69	0.60 ± 0.12
43.5	0.53	0.65	0.52	0.55	0.62	0.57 ± 0.06
$\gamma_i \pm s_{\gamma_i}$	0.52 ± 0.01	0.70 ± 0.06	0.56 ± 0.06	0.51 ± 0.06	0.66 ± 0.05	

Statistical procedure of the *F*-tests:

$$\bar{\gamma} = \sum_{i,T} \gamma_{i,T}/n = 0.59;$$

$$s^2_{tot.} = \sum_{i,T} (\gamma_{i,T} - \bar{\gamma})^2/(n-1) = 0.0078 \text{ [9 degrees of freedom } (DF)].$$

Influence of temperature on γ:

$$s^2_p = \sum_T DF_T s^2_{\gamma_T}/\sum_T DF_T = 0.0360\ (DF = 8);$$

$$F_T = s^2_{tot.}\ (DF = 9)/s^2_p\ (DF = 8) = 0.22, \textit{i.e.}, \text{ non-significant.}$$

Influence of group i on γ:

$$s^2_p = \sum_i DF_i s^2_{\gamma_i}/\sum_i DF_i = 0.0027\ (DF = 4);$$

$$F_i = s^2_{tot.}\ (DF = 9)/s^2_p\ (DF = 4) = 2.89, \textit{i.e.}, \text{ non-significant.}$$

Mean value of $\gamma = 0.59 \pm 0.03$.

tests show that γ is independent of group i and of temperature. The mean value of $\gamma = 0.59 \pm 0.03$ has been used in further calculations. The value of γ is within error equal to that of ODS-silica ($\gamma = 0.61 \pm 0.05$) reported previously[2]. Obviously the CNA monomers, like water adsorbed on to bare silica, promote eluent localization on the silica beneath the CNA layer. It is assumed that γ is independent of the eluent strength.

Solute localization and intramolecular electronic effects

The parameters β, δ and ϱ_k have been estimated from eqn. 5 for a number of *m*- and *p*-substituted phenols, nitrobenzenes, benzaldehydes, anilines and pyridines in *n*-hexane, the binary eluent and methylene chloride. The $\log(V_N/W)$ data for these solutes are given in Table IV. The required variables in eqn. 5 are collected in Table I. Multiple regression analyses of the data (left-hand side of eqn. 5) show that σ rather than σ^- constants[8] have to be used to obtain the best fit to the experimental data, except for the phenols. The adsorption behaviour of *p*-hydroxybenzaldehyde appears to be anomalous and therefore its data were excluded from the regression analyses.

The values of β obtained are given in Table V. A variance analysis[2] applied to these data (the nitrobenzenes were excluded from this analysis because their β values are based on only one degree of freedom) shows that β is not significantly dependent

TABLE IV

LOG (V_N/W) DATA FOR MONOSUBSTITUTED PHENOLS, ANILINES, PYRIDINES, BENZALDEHYDES AND NITROBENZENES IN *n*-HEXANE (H, $\varepsilon^\circ = 0.0$), *n*-HEXANE–METHYLENE CHLORIDE (65:35) (B, $\varepsilon^\circ = 0.22$) AND METHYLENE CHLORIDE (C, $\varepsilon^\circ = 0.32$) AT 25° AND 43.5°.

i	*i*-ØOH		*i*-ØNH$_2$		*i*-C$_5$H$_5$N		*i*-ØCHO		*i*-ØNO$_2$	
	B, 43.5°	*C*, 25°	*B*, 43.5°	*C*, 25°	*B*, 43.5°	*C*, 25°	*H*, 25°	*B*, 25°	*H*, 25°	*B*, 25°
H	0.97	0.58	0.97	0.41	1.85	1.56	1.40	0.30	0.85	−0.17
m-F	1.00	0.53	0.72	0.12						
p-F	1.01	0.67	1.03	0.47						
m-Cl	0.98	0.71	0.68	0.10	1.10	0.84	1.22	0.16	0.70	−0.26
p-Cl	1.00	0.68	0.85	0.24			1.35	0.27	0.71	−0.23
m-Br	1.00	0.76	0.67	0.08	1.17	0.81				
p-Br	1.02	0.71	0.83	0.21						
m-CH$_3$	0.96	0.55	0.94	0.46	1.94	1.54				
p-CH$_3$	0.98	0.57	1.13	0.45	2.13	1.70	1.55	0.38		
m-OCH$_3$	1.34	0.87	1.33	0.64			2.02	0.53		
p-OCH$_3$	1.41	0.84	1.67	0.99			2.30	0.81	1.69	0.22
m-NO$_2$	1.64	1.27	1.01	0.19			2.26	0.66	1.90	0.34
p-NO$_2$	1.88	1.36	1.19	0.22			2.30	0.66		
m-CN	1.94	1.23	1.34	0.47	1.61	1.04				
p-CN	2.04	1.46	1.33	0.38	1.65	1.11				
m-CHO	1.93	1.42								
p-CHO	2.25	1.69								
m-CO$_2$CH$_3$	1.84	1.23								
p-CO$_2$CH$_3$	1.94	1.37								
m-COCH$_3$	2.16	1.48	1.93	1.02						
p-COCH$_3$	2.37	1.78	2.00	1.04						

TABLE V

VALUES OF β, ϱ, δ AND THE STANDARD ERROR OF FIT (s) OF MONOSUBSTITUTED PHENOLS, NITROBENZENES, BENZALDEHYDES, ANILINES AND PYRIDINES IN *n*-HEXANE (H), *n*-HEXANE–METHYLENE CHLORIDE (65:35) (B) AND METHYLENE CHLORIDE (C) AT 25° AND 43.5°

Parameter	*Solute series*	*H, 25°*	*B, 25°*	*B, 43.5°*	*C, 25°*
$\beta \pm s_\beta$	Phenols (σ)			0.43 ± 0.05	0.49 ± 0.08
	Phenols (σ^-)			0.48 ± 0.04	0.51 ± 0.07
	Nitrobenzenes	(0.75 ± 0.04)	(0.76 ± 0.06)		
	Benzaldehydes	0.31 ± 0.13	0.70 ± 0.17		
	Anilines			0.43 ± 0.07	0.46 ± 0.06
	Pyridines			0.44 ± 0.16	0.56 ± 0.15
$\varrho \pm s_\varrho$	Phenols (σ)			0.61 ± 0.15	1.13 ± 0.28
	Phenols (σ^-)			0.56 ± 0.10	0.82 ± 0.16
	Nitrobenzenes	(−0.44 ± 0.04)	(−0.66 ± 0.06)		
	Benzaldehydes	−0.77 ± 0.18	−0.38 ± 0.23		
	Anilines			−1.45 ± 0.18	−1.76 ± 0.16
	Pyridines			−3.38 ± 0.38	−3.03 ± 0.35
$\delta \pm s_\delta$	Phenols (σ)			0.19 ± 0.05	0.21 ± 0.10
	Phenols (σ^-)			0.20 ± 0.04	0.30 ± 0.09
	Nitrobenzenes	(−0.01 ± 0.02)	(0.16 ± 0.03)		
	Benzaldehydes	0.13 ± 0.09	0.21 ± 0.13		
	Anilines			0.24 ± 0.07	0.29 ± 0.06
	Pyridines			0.06 ± 0.12	−0.08 ± 0.11
s	Phenols (σ)			0.16	0.24
	Phenols (σ^-)			0.13	0.21
	Nitrobenzenes	(0.09)	(0.04)		
	Benzaldehydes	0.15	0.27		
	Anilines			0.19	0.16
	Pyridines			0.21	0.19

on temperature, the eluent or group k. With respect to localization phenomena, CNA- and ODS-silica are similar: β (CNA-silica) = 0.48 ± 0.04 whereas β (ODS-silica) = 0.51 ± 0.03 (ref. 2).

The ϱ values are given in Table V. The positive ϱ value of the phenols indicates that the phenolic hydroxyl group is an electron acceptor towards the silanol groups of the CNA-silica. Benzaldehydes, anilines and pyridines are electron donors towards CNA-silica as their ϱ values are negative. The same holds for nitrobenzenes, although it should be noted that the result for this series is based on only one degree of freedom. The absolute value of ϱ_k increases with increasing Q_k^0 (proton acceptor strength). The improved fit obtained on using σ^- instead of σ parameters for the phenols (compare the s values in Table V) points to mesomeric interaction between group i and the phenolic hydroxyl group, which can be expected if group i is a *para*-substituent. If, in addition, group i can be adsorbed flatly, *i.e.*, without disturbing the conjugated system of double bonds in the adsorbate, and group i and k are Lewis base and Lewis acid groups towards silica, respectively, anomalously strong adsorption can be expected. These conditions are fulfilled by *p*-hydroxybenzaldehyde. When σ parameters are used, the experimental $\log(V_N/W)$ values of this solute are about 0.47 larger than predicted, whereas the use of σ^- constants reduces this discrepancy to 0.28 in the binary eluent

and to 0.09 in methylene chloride. Similar results have been obtained for ODS-silica[2]. However, contrary to ODS-silica, where intramolecular electronic effects depend strongly on the eluent strength, the ϱ_k values on CNA-silica are only slightly affected by the polarity of the eluent.

Probably, the polar cyano groups of the bonded phase play a predominant role in the stabilization of the (polar) solute–adsorbent complex. On ODS-silica this stabilization can only be due to the increased (bulk) eluent strength.

In most instances, the δ values are about equal for CNA- and ODS-silica. The physical meaning of δ is obscure. Probably δ should be ascribed to secondary eluent effects, *i.e.*, solute–eluent interactions.

Polycyclic aromatic hydrocarbons

The experimental $\log(V_N/W)$ data are given in Table VI, together with the experimental S^0 and A_s values, obtained from eqns. 6 and 1, and the theoretical A_s data, calculated by eqn. 7.

TABLE VI

LOG (V_N/W) DATA FOR SOME POLYCYCLIC AROMATIC HYDROCARBONS IN *n*-HEXANE (H) AND *n*-HEXANE–METHYLENE CHLORIDE (65:35) (B) AT 25°, THEIR EXPERIMENTAL $S°$ AND A_s VALUES ON CNA-SILICA, AND CALCULATED A_s VALUES

Solute	*No.*	*H, 25°*	*B, 25°*	$S°$	A_s	A_s *(calc.)*
Benzene	1	−0.29	−*	1.45		6.0
Naphthalene	2	−0.06	−0.60	1.98	5.6	8.1
Acenaphthene	3	0.00	−*	2.11		9.7
Diphenyl	4	0.05	−0.64	2.23	7.1	9.7
Fluorene	5	0.183	−0.50	2.53	7.1	9.9
Bibenzyl	6	0.232	−0.66	2.64	9.2	12.4
Anthracene	7	0.223	−0.58	2.62	8.3	10.2
Phenanthrene	8	0.232	−0.48	2.64	7.4	10.2
Pyrene	9	0.293	−0.50	2.78	8.2	10.7
Fluoranthene	10	0.324	−*	2.85		10.7
Chrysene	11	0.509	−0.47	3.27	10.1	12.3
p-Terphenyl	12	0.408	−0.55	3.04	9.9	13.4
3,4-Benzpyrene	13	0.592	−0.45	3.46	10.8	12.8
Perylene	14	0.636	−0.35	3.56	10.2	12.8
Coronene	15	0.768	−0.31	3.86	11.1	13.8
p,p'-Quaterphenyl	16	0.821	−0.53	3.98	14.0	17.1

* V_N values are very small.

Eqn. 6 fits the S^0 values with $\zeta = 0.105 \pm 0.005$ (Fig. 2). The data point 6 (bibenzyl) has been excluded from this calculation because bibenzyl shows anomalous adsorption behaviour on to bare silica and ODS-silica. The ζ value obtained on CNA-silica is slightly larger than that on ODS-silica ($\zeta = 0.095 \pm 0.004$), but smaller than that on bare wide-pore silica ($\zeta = 0.14$). These small ζ values are due to the increased homogeneity of the silica resulting from the elimination of the reactive silanol groups, to which polycyclic arenes adsorb preferentially[12]. None of the data points deviates significantly from the line in Fig. 2. This seems to indicate flat adsorption, even of the non-planar polyphenyls and of coronene (diameter about 9 Å).

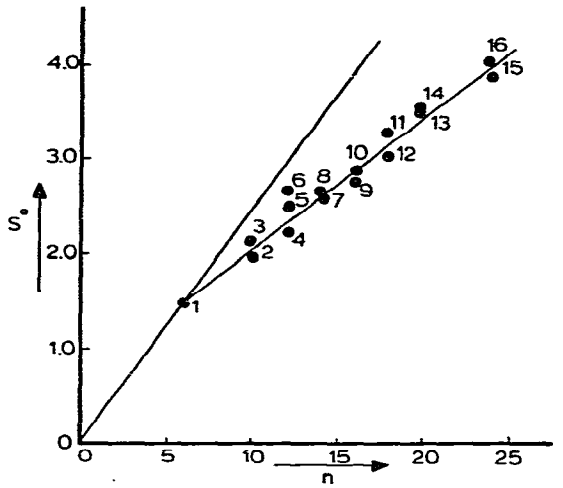

Fig. 2. Experimental $S°$ values for some polycyclic aromatic hydrocarbons *versus* the number of aromatic carbon atoms (n) on CNA-silica (the data point 6 is excluded from the calculation of the regression line). Eluent: n-hexane (25°). Numbering of the data points according to Table VI.

However, the experimental A_s values are smaller than expected from eqn. 7 and show a mean deviation of $\Delta A_s = -2.5 \pm 0.4$ from A_s (calc.) data. As on ODS-silica the experimental and calculated A_s values are about equal, it may be that the slightly larger ζ and the smaller A_s values on CNA-silica are related. It can be estimated (see Appendix) that in n-hexane about 90% of the CNA groups are adsorbed on to silanol sites. Therefore, it can be expected that parts of these extended and non-localized adsorbate molecules cover CNA monomers on adsorption. If this supposition is true the average adsorbate–silica distance (and hence ζ) will be increased and less eluent molecules are desorbed on adsorption of a solute molecule in the binary eluent.

Hexyl and cyclohexyl derivatives

The $\log(V_N/W)$ data for the examined monosubstituted (cyclo)hexyl compounds are given in Table VII. The adsorbent parameters obtained with this solute series ($\alpha = 0.48 \pm 0.02$ and $\log V_a = -1.10 \pm 0.08$) deviate slightly from those obtained with monosubstituted (chloro)benzenes. This may be due to the selectivity of CNA-silica towards cyano and aldehyde solute groups, as mentioned before, which will significantly affect the adsorbent parameters in the (cyclo)hexane series.

The numbers of adsorbed methylene groups in the binary eluent (m) at 25°, obtained from eqn. 8, are given in Table VII. The average m values for hexanes and cyclohexanes are 4.7 ± 0.6 and 4.8 ± 2.0, respectively. On ODS-silica these m values are 2.5 ± 1.0 and 5.0 ± 2.5, respectively. Snyder[3] reported $m = 2.9$ for hexylbenzene on bare silica. Neither the α nor the m value obtained for the solute series indicates hindrance of adsorption by the CNA groups.

TABLE VII

LOG (V_N/W) DATA FOR SOME MONOSUBSTITUTED HEXANES AND CYCLOHEXANES IN *n*-HEXANE (H) AND *n*-HEXANE–METHYLENE CHLORIDE (65:35) (B) AT 25°, AND THE NUMBER OF ADSORBED METHYLENE GROUPS (m)

Compounds	*Substituent*	*H, 25°*	*B, 25°*	*m*
Hexanes	Cl	−0.32	−*	
	Br	−0.23	−*	
	SH	−0.25	−0.97	5.2
	CHO	1.29	0.32	4.2
	CO_2CH_3	1.50	0.36	4.7
Cyclohexanes	Cl	−0.31	−*	
	Br	−0.33	−*	
	SH	−0.09	−0.79	5.1
	CN	1.51	0.37	6.7
	CO_2CH_3	1.31	0.35	2.8

* V_N values are very small.

CONCLUSIONS

The adsorption theory of Snyder gives a good description of the retention data on the investigated CNA-silica, when the parameters in this model are adjusted for the deactivation of the silica by the amination reaction.

The effective adsorbent activity, α, strongly decreases (to 0.44) as a result of preferential deactivation of reactive silanol groups and due to a small contribution of the CNA groups to the eluent strength of *n*-hexane. Solute adsorption is controlled by enthalpic interaction forces. The effective contributions of solute and eluent localization can be described by Snyder's theory with a parameter $\beta = 0.48$ for the former and a parameter $\gamma = 0.59$ for the latter effect. The magnitude of both parameters are within error equal to those on ODS-silica.

Intramolecular electronic effects on the adsorption of *m*- and *p*-substituted phenols, nitrobenzenes, benzaldehydes, anilines and pyridines to CNA-silica can be described satisfactorily with Hammett's relationship. The aldehyde group shows strong mesomeric interaction with the phenolic hydroxyl group. The susceptibility for induced charge shifts caused by substituents increases with increasing proton acceptor strength of the reactive solute group. The increase in this susceptibility with increasing eluent strength, found on ODS-silica, is not significant on CNA-silica, owing to the polar CNA groups near the silica surface.

All of the results obtained indicate flat adsorption of the solutes to the silica surface beneath the CNA groups, except those of polycyclic hydrocarbons. The solutes probably show slightly skewed adsorption due to the shielding effect of adsorbed CNA groups.

The CNA-silica shows a significant selectivity towards cyano and aldehyde solute groups.

ACKNOWLEDGEMENTS

The authors are indebted to Mr. P. A. Elberse and Drs. L. A. M. Hermans for their accurate BET measurements on Merckosorb Si 100.

APPENDIX

The estimation of the contribution of a polar monomeric bonded phase to the solvent strength in the boundary layer is difficult and needs some approximations. The basic assumption in the proposed procedure is that the bound monomers can be treated like solute molecules of the type i–$(CH_2)_p$–k, where group k is a strongly localized group and the polar group i is partly delocalized (it is assumed that $Q_k^0 = 6$). The $f(Q_k^0)_p$ values for several values of p are given by Snyder[3]. As group k is chemically bound, its lateral mobility is very small. This is accounted for by setting $\beta = 1$, *i.e.*, equal to β on alumina where the field strength of the sites (partly buried aluminium atoms) falls off rapidly from their centres.

The "adsorption coefficient" of isolated $(CH_2)_p$–i groups in eluent e is given by the equation

$$\log K = \log\left(\frac{N_{i,\,\mathrm{ads}}}{N_i}\right) = \log\left(\frac{n_{i,\,\mathrm{ads}}}{n_i/z}\right) = \alpha[Q_i^0 - \beta f(Q_k^0)_p\, Q_i^0 - \varepsilon_e^0\, A_s] \tag{9}$$

where $N_{i,\,\mathrm{ads}}$ and N_i are the molar fractions of i in the adsorbed monomolecular surface layer of the eluent and in the z non-sorbed eluent layers immediately above it, respectively; $n_{i,\,\mathrm{ads}}$ and n_i are the corresponding numbers of moles of monomers (per square metre) in the first and the adjacent z monolayers of eluent, respectively. The latter can be estimated from the equation

$$n_i\,(\mathrm{per\ m^2}) = \frac{z\,N_i\,V_a}{A\,\overline{V}} \approx \frac{z\,N_i\,V_a}{A\,V_e} = \frac{35 \cdot 10^{-5}\,z\,N_i}{V_e} \tag{10}$$

where $\overline{V}$ and V_e are the (mean) molar volumes of the surface layer and of the eluent, respectively. As $(n_{i,\,\mathrm{ads}} + n_i)$ is equal to the known surface concentration $c_i(\mathrm{mole/m^2})$, N_i can be expressed as a function of K and z:

$$N_i = c_i\,V_e/[35 \cdot 10^{-5}\,(K + z)] \tag{11}$$

The A_s value of the monomer is given by eqn. 8. The (hypothetical) eluent strength of a layer of delocalized $(CH_2)_p$–i groups can be estimated from the equation

$$\varepsilon_i^0 = [Q_i^0 - \beta f(Q_k^0)_p\, Q_i^0]/A_s \tag{12}$$

The eluent strength of a binary eluent i–e (ε_{ie}^0) is given by Snyder[3]:

$$\varepsilon_{ie}^0 = \varepsilon_e^0 + \frac{\log[N_i \cdot 10^{\alpha A_s(\varepsilon_i^0 - \varepsilon_e^0)} + 1 - N_i]}{\alpha\,A_s} \tag{13}$$

Using $\alpha = 0.51$ in eqns. 9 and 13 and $\gamma = 0.61$ in eqn. 8 (obtained on ODS-silica, to be considered as a reference adsorbent) and substituting values of N_i, A_s, ε_i^0 and ε_e^0 in eqn. 13 gives ε_{ie}^0 values for combinations of m and z. It should be noted that m and z are mutually dependent, which restricts the number of relevant (m, z) combinations to be examined for any particular bonded phase (Fig. 3). The ε_{ie}^0 values for possible (m, z) combinations on CNA-silica [$1.25 \cdot 10^{-6}$ mole/m^2, $f(Q_k^0)_{p=2} = 0.57$ (ref. 3)] and

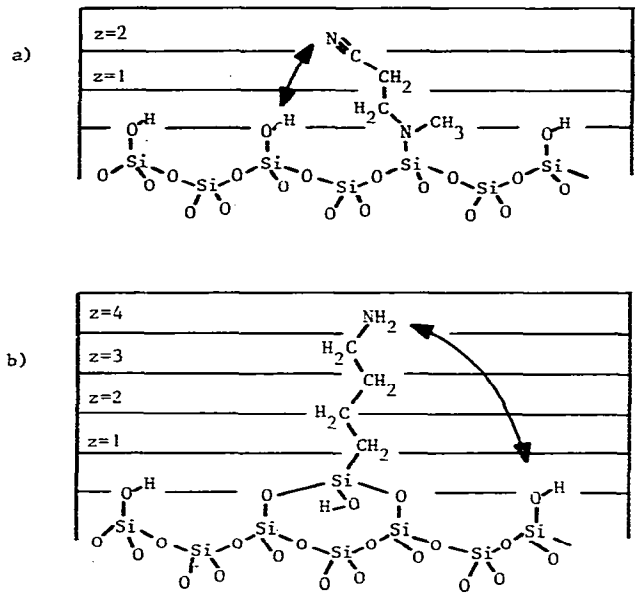

Fig. 3. Orientation of (a) CNA and (b) ABS monomers bound to silica for $z = 2$ ($m = 1$) and $z = 4$ ($m = 0$), respectively.

4-aminobutylsilyl-(ABS-) silica [$2.54 \cdot 10^{-6}$ mole/m^2, $f(Q_k^0)_{p=4} = 0.47$ (ref. 3)] in *n*-hexane ($\varepsilon_e^0 = 0$) are given in Table VIII. If it is assumed that all monomer configurations have an equal chance of occurring, ε^0 (CNA:hexane) = 0.04 and ε^0 (ABS:hexane) = 0.09. The accuracy of these data is about 0.02, *i.e.*, equal to that of eqn. 13 for conventional binary eluents[3]. The corresponding fractions of adsorbed monomers are 0.88 (CNA) and 0.95 (ABS). The $\log(V_N/W)$ data for monosubstituted benzenes can be described by eqn. 1 using experimental $\log V_a$ values on both adsorbents, $\alpha = 0.51$ (ODS-silica) and $\varepsilon_{ie}^0 = 0.05$ (CNA: hexane) or $\varepsilon_{ie}^0 = 0.08$ (ABS:hexane). These data are in good agreement with the theoretical estimates. Similar calculations reveal that the increase in ε^0 of methylene chloride by the CNA monomers is not significant ($\Delta\varepsilon_e^0 = 0.004$), whereas the ABS group increases the eluent strength by about 0.03 in methylene chloride. Intermediate $\Delta\varepsilon_e^0$ values can be expected for *n*-hexane–methylene chloride mixtures.

TABLE VIII

CALCULATED ε_{ie}^0 VALUES ON CNA-SILICA AND ABS-SILICA FOR PLAUSIBLE (m,z) COMBINATIONS IN *n*-HEXANE

m	ε_{ie}^0 (CNA:hexane)		ε_{ie}^0 (ABS:hexane)			
	$z = 1$	$z = 2$	$z = 1$	$z = 2$	$z = 3$	$z = 4$
			0.10	0.10	0.09	0.09
1	0.04	0.04	0.09	0.09	0.08	
2	0.04		0.08	0.08		
3			0.07			

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