Journal of Chromatography, 461 (1989) 243–258
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1448

ROLE OF UNREACTED SILANOLS IN THE ADSORPTION PROPERTIES OF DERIVATIZED SILICA

GYÖRGY FÓTI, CRISTINA MARTINEZ and ERVIN sz. KOVÁTS*
Laboratoire de Chimie Technique de l'École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne (Switzerland)

SUMMARY

The adsorbents studied were samples of a precipitated silica, covered with a dense layer of (3,3-dimethylbutyl)dimethylsiloxy-, (5-cyano-3,3-dimethylpentyl)-dimethylsiloxy- and tetradecyldimethylsiloxy- substituents. Deuteration of unreacted silanols across the graft was investigated, using dilute solutions of hydroxy-deuterated water, methanol and ethanol in acetonitrile. Excess adsorption isotherms of the solutes were also determined. The results suggest that access to all silanols is sterically hindered by the surface substituents but to different extents. They are accessible in a time average through occasional holes in the graft, formed by the lateral vibrational motion of the substituents.

INTRODUCTION

At the interface between silica, covered with an organyl-dimethylsiloxy monolayer that is as dense as possible, and a dilute solution of water in acetonitrile, the protons of the unreacted silanols have been shown to be easily accessible for isotope exchange across the graft[1,2]. This has been demonstrated by performing breakthrough experiments with water and deuterium oxide solutions on a chromatographic column packed with the grafted silica[1]. Based on the theory of the chromatographic process[3], the results permit the calculation of the surface concentration of the silanols accessible for $H/^2H$ exchange. Using a silica modified with the same grafts as in this work, it has been shown that the extent of $H/^2H$ exchange is independent of the linear flow-rate of the mobile phase at values $u_\mu < 0.6$ cm/s, and at these flow-rates it is also independent of the temperature between 20 and 80°C[2]. It has therefore been concluded that under normal experimental conditions ($u_\mu \approx 0.3$ cm/s; $T_c = 20.0$°C) all silanols exchange across the graft.

The sum of the surface concentration of reacted and unreacted silanols was the same on all adsorbents, amounting to

$$\Gamma_{OH,u} + \Gamma_{sox} = 8.44 \pm 0.10\ \mu mol/m^2 \tag{1}$$

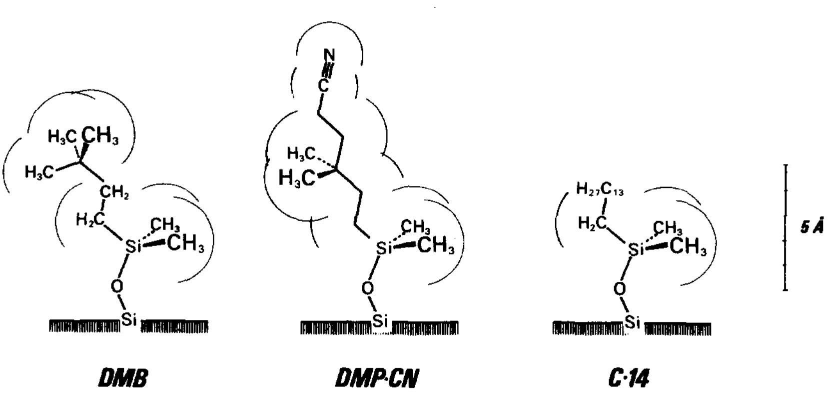
where $\Gamma_{OH,u}$ is the surface concentration of unreacted silanols and Γ_{sox} is that of the organyl-dimethylsiloxy graft. This result is considered to be representative of the surface concentration of silanols on precipitated silicas. (The term "precipitated silica" refers to samples prepared in the usual way by acidification of a water-glass solution; see ref. 4, p. 554.) Eqn. 1 shows that on adsorbents usually applied in liquid–solid chromatography (Γ_{sox} = 3.6–4.2 μmol/m^2) an amount of about $\Gamma_{\mathrm{OH,u}} \approx 4.5$ μmol/m^2 of unreacted silanols is present at the surface under the graft.

The same experiments also permitted the evaluation of points on the adsorption isotherm of water at low water concentrations. It has been repeatedly reported that water is preferentially adsorbed in this domain by grafted silicas[5–7]. In fact, at low volume fractions, $\varphi_{\mathrm{w}} < 0.01$, the isotherm is characterized by a positive water adsorption, which already increases to a saturation value at $100\varphi_{\mathrm{w}}$ = 0.2–0.3% (v/v)[2]. Therefore, it has been proposed that on the non-polar surface there are specific adsorption sites, one site accommodating one water molecule. Application of the Everett–Klinkenberg[8,9] equation to the description of the isotherm gave $\Gamma_{\mathrm{Siol}} = 0.7$ μmol/m^2 for water adsorption on silicas covered by the densest organyl-dimethylsiloxy layer; the subscript Siol refers to the hypothesis that these sites are silanols available for the adsorbate.

In summary, it has been shown that about 15% of the unreacted silanols are active for water adsorption. These silanols could be at particular positions with easy accessibility for components capable of forming hydrogen bonds. In a second extreme picture, every silanol might be accessible 15% of the time, owing to the vibrational motion of the graft.

In this paper, the accessibility of silanols for H/^{2}H exchange and for adsorption in dilute solutions of methanol and of ethanol is examined. It will be shown that the results are compatible with a model where the unreacted silanols are all sterically hindered so that their adsorption activity largely depends on the size of the adsorbate. Only a negligible proportion of the silanols is accessible without being sterically hindered.

The same chemically modified adsorbents were applied as in ref. 2 (see Fig. 1), grafted on two different batches of the same precipitated silica. The first adsorbent was covered by a dense layer of (3,3-dimethylbutyl)dimethylsiloxy (DMB) groups. The



DMB ***DMP·CN*** ***C·14***

Fig. 1. The (3,3-dimethylbutyl)dimethylsiloxy (DMB), (5-cyano-3,3-dimethylpentyl)dimethylsiloxy (DMP · CN) and tetradecyldimethylsiloxy (C · 14) substituents.

surface of this adsorbent was shown to be non-polar and non-swellable; in the dense layer the dimethylmethylene base and the *tert.*-butyl head doubly shield the underlying matrix. The second adsorbent was a derivative of the DMB substituent. At the surface, covered by the (5-cyano-3,3-dimethylpentyl)dimethylsiloxy (DMP · CN) substituents, cyano groups are exposed. The surface is efficiently shielded by groups of bulky substituents, similar to the case with the DMB group. Finally, a tetradecyldimethylsiloxy (C · 14)-modified surface was chosen as an example of a long-chain covered surface. The C · 14-covered silica was preferred to the widely used C · 18-graft, because the latter shows a phase transition at about 15 ± 10°C; hence the graft is not in a well defined state at 20°C, the temperature often used in our experiments[10,11]. All adsorbents were covered with as dense a layer as possible[12–14], in contrast to the work reported in ref. 2, where the DMP · CN coverage was only about 92% of the maximum density. For surface concentrations, see Table I.

CALCULATIONS

The surface concentration of accessible unreacted silanols and that of the excess adsorption isotherm at low protic solute concentrations in acetonitrile is based on a series of breakthrough experiments. The underlaying theory is outlined in ref. 3 and is discussed in detail in ref. 2. In summary, on a chromatographic column packed with the grafted silica, first the breakthrough volume of a dilute solution of the protic solute was measured on the column containing dry acetonitrile, $V_R^{(0)}$ then, after equilibrium, the breakthrough volume of a dilute solution of the hydroxy-deuterated solute was determined to give V_R^*. The volume of the protic solute having the same number of exchangeable protons as those which were accessible at the surface for H/^{2}H exchange was calculated with the equation

$$V_{\kappa,\mathrm{exch}}\,(\mathrm{su}) = \varphi_{\mathrm{su}}[V_R^*(\mathrm{su}) - V_R^{(0)}(\mathrm{su})] \tag{2}$$

where $V_{\kappa,\mathrm{exch}}$ (su) is called the exchange capacity and φ_{su} is the volume fraction of the solute in acetonitrile. The surface concentration of the protons accessible by the protic solute for H/^{2}H exchange is given by

$$\Gamma_{\mathrm{OH,acc}}\,(\mathrm{su}) = zV_{\kappa,\mathrm{exch}}(\mathrm{su})/v_{\mathrm{su}}S \tag{3}$$

where z is the number of exchangeable protons in the solute ($z = 1$ for CH_3OH and C_2H_5OH and $z = 2$ for H_2O), v_{su} is the partial molar volume of the solute and S is the surface area of the adsorbent in the column.

The experiments were completed by determining the breakthrough volume of labelled acetonitrile on the column filled with acetonitrile. This retention volume was assumed to measure the hold-up volume, $V_{\mu/\mathrm{vNA}}$, of the system, where the subscript vNA refers to the specific Gibbs convention "*N*othing is *A*dsorbed in terms of *v*olumes", defined in the equation

$$\Psi_{\mathrm{su}} + \Psi_{\mathrm{AN}} = 0 \tag{4}$$

where Ψ is the adsorption in terms of volume per unit surface area and the subscripts su and AN represent solute and acetonitrile, respectively[3]. Points on the adsorption isotherm were calculated with the equation

$$S\Psi_{\mathrm{su/vNA}} = \varphi_{\mathrm{su}}[V_{\mathrm{R}}^{(0)}(\mathrm{su}) - V_{\mu/\mathrm{vNA}}] \tag{5}$$

If the Everett–Klinkenberg equation:

$$\Psi_{\mathrm{su/vNA}} = \frac{\varphi_{\mathrm{su}}\varphi_{\mathrm{AN}}}{b + c\varphi_{\mathrm{su}}} \tag{6}$$

is applicable (specific sites with strong adsorption affinity for the solute), the constants b and c can be determined from the linear plot of the equation

$$S\varphi_{\mathrm{AN}}/[V_{\mathrm{R}}^{(0)}(\mathrm{su}) - V_{\mu/\mathrm{vNA}}] = b + c\varphi_{\mathrm{su}} \tag{7}$$

From eqn. 6, is seen that $1/b$ is the slope of the isotherm at $\varphi_{\mathrm{su}} = 0$ and that $1/c$ is the limiting adsorption capacity of the surface for the solute where all sites accommodate a solute molecule. These sites will be identified as silanols accessible for solute adsorption. Their surface concentration in terms of moles per unit surface area is given by

$$\Gamma_{\mathrm{Siol}} = 1/cv_{\mathrm{su}} \tag{8}$$

where v_{su} is the partial molar volume of the solute.

In eqns. 2–8, a knowledge of the partial molar volume of the solute at high dilution, v_{su}, and the surface area of the adsorbent in the column, S, is necessary. The partial molar volume is nearly constant in the experimental domain investigated and can be calculated from the molar volume of the pure solute, v_{su}^0, as follows:

$$v_{\mathrm{su}} = f_{\mathrm{su/AN}}\, v_{\mathrm{su}}^0 \qquad \text{for } \varphi_{\mathrm{su}} \rightarrow 0 \tag{9}$$

The value of $f_{\mathrm{H_2O/AN}} = 0.933$ was taken from ref. 15; the factors for methanol ($f_{\mathrm{CH_3OH/AN}} = 0.988$) and ethanol ($f_{\mathrm{C_2H_5OH/AN}} = 0.999$) were determined experimentally. These values, valid at 20.0°C, were used at all temperatures. The surface area of the adsorbent in the column was calculated on the basis of results reported in ref. 16. It has been shown that the surface area of grafted silica is nearly the same as that of the silica part in the adsorbent. The surface area of the adsorbent is therefore calculated from the molar volume of the pure solute, v_{su}^0, as follows:

$$S = m(\mathrm{SiO_2})s \tag{10}$$

where s is the specific surface area of the precipitated silica used as starting material. The mass of the silica in the column was calculated with the equation

$$m(\mathrm{SiO_2}) = m\theta\{1 + 10^{-6}\,\Gamma_{\mathrm{sox}}s[M(\mathrm{R}) - corr]\}^{-1} \tag{11}$$

TABLE I

CHARACTERISTICS OF THE STATIONARY PHASES AND COLUMNS USED

The symbol Γ_{sox} represents the surface concentration of the organyl-dimethylsiloxy substituent, $m(\mathrm{SiO_2})$ is the weight of the silica part of the stationary phase, S is the surface area of the adsorbent in the column and $V_{\mu/v\mathrm{NA}}$ is the void volume, identified as the breakthrough volume AN → AN*. The DMB- and C · 14-covered adsorbents were prepared with batch 1 (s = 298 $\mathrm{m^2/g}$) and the DMP · CN-covered sample with batch 2 (s = 291 $\mathrm{m^2/g}$) of LiChrosorb Si 100. Standard deviations are given in the bottom row.

Stationary phase		*Column*			
Graft	Γ_{sox} ($\mu mol/m^2$)		$m(SiO_2)$ (g)	S (m^2)	$V_{\mu/vNA}$ (ml)
DMB	3.90	A	1.162	346	5.11
		B	1.137	339	5.37
DMP · CN	3.96	A	1.257	366	5.28
		B	1.259	366	5.20
C · 14	4.08	A	1.172	349	5.02
		B	1.169	348	5.14
S.D.	0.02		0.002	4	0.02

where $m\theta$ is the mass of the grafted adsorbent in the column, Γ_{sox} ($\mu\mathrm{mol/m^2}$) is the surface concentration of the graft, $M(\mathrm{R})$ is the molecular weight of the organyl-dimethylsilyl radical and $corr = 2.5$ is a correction for adsorbed water on the original silica lost and for proton substituted during silylation. The characteristics of the columns used in this study are listed in Table I.

EXPERIMENTAL

General

Silicon dioxide samples were stored and handled in a dry box (< 1 ppm of oxygen and water). Elemental analyses were made with a Perkin-Elmer Model 240 B apparatus. Nitrogen adsorption isotherms were measured with a slightly modified Sorptomatic 1800 apparatus from Carlo Erba (Milan, Italy)[17]. For further details, see refs. 2 and 18.

Materials

The precipitated silica used as starting material was batches 1 and 2 of LiChrosorb Si 100 from Merck (Darmstadt, F.R.G.) with a nominal grain diameter $d_{\mathrm{gr}} = 10$ μm. BET evaluation of the nitrogen adsorption isotherm in the domain $0.05 < P_e/P_0 < 0.23$ gave a specific surface area of 298 ± 3 $\mathrm{m^2/g}$ for batch 1 and 291 ± 3 $\mathrm{m^2/g}$ for batch 2. Nitrogen for adsorption experiments (99.999%) and liquid nitrogen for thermostating (99.8%) were obtained from Carbagas (Lausanne, Switzerland). The silylating agents, N-[(3,3-dimethylbutyl)dimethylsilyl]-N,N-dimethylamine, N-[(5-cyano-3,3-dimethylpentyl)dimethylsilyl]-N,N-dimethylamine and N-(tetradecyldimethylsilyl)-N,N-dimethylamine, were synthesized in our laboratory[12].

Eluent

Commercial high-performance liquid chromatographic (HPLC)-grade acetonitrile (AN) from Ammann Technik (Kölliken, Switzerland) was refluxed with phosphorus pentoxide (5.5 g for 1.5 l of acetonitrile) for 30 min and then distilled, discarding the first and last fractions of 10%. Karl Fisher titration of the distilled product gave a water content of $-0.0017 \pm 0.0065\%$ (w/w), corresponding to a maximum water content of 0.0048% ($100\varphi_W = 0.0038$).

Doubly distilled water was prepared by distilling deionized water over potassium permanganate. HPLC-grade methanol from Ammann Technik, research-grade ethanol from Fluka (Buchs, Switzerland), research-grade ^2H_2O, CH_3O^2H, $C_2H_5O^2H$ and C^2H_3CN from Chemische Fabrik Uetikon (Uetikon, Switzerland) (isotope purity > 99.5%) were used without purification.

Eluents of the appropriate composition were prepared by weighing. The volume fractions of solution pairs for isotope-exchange experiments with labelled and unlabelled solute did not differ by more than $100\Delta\varphi \approx 0.002$. Labelled acetonitrile was prepared by dissolving about 1.0% (w/w) [$^2H_3$]acetonitrite in acetonitrile. All eluents were degassed immediately before use in the bottle connected to the pump inlet by bubbling helium through the mixture. During the experiments, the mixture was kept under a slight helium overpressure (0.07 bar).

Chromatographic columns

Column materials were prepared by allowing vacuum-dried LiChrosorb Si 100 to react with the appropriate R-dimethyl(dimethylamino)silane at 180°C for 100 h, following the procedure in ref. 12. The DMB- and C · 14-covered adsorbents were prepared with batch 1 and the DMP · CN-covered sample with batch 2. For surface concentrations, Γ_{sox}, calculated from elemental analysis, see Table I.

The preparation of the columns is described in details in ref. 18. The columns were stainless-steel tubes (25.0 cm × 4.00 mm I.D.) and were packed by the slurry method (slurry in 2-propanol), then the column bed was compacted with pure methanol (C · 14) or with methanol containing 1% (w/w) of potassium bromide at 500 bar for 45 min. Two columns were packed with each adsorbent. The columns were dried after preparation at 120°C in an argon stream, and the mass of the stationary phase in the column, m_θ, was determined by weighing. The mass of silica in each column, $m(SiO_2)$, calculated with eqn. 11, is listed in Table I.

Apparatus

The solvent selector inlet of a Model 510 pump from Waters Assoc. (Milford, MA, U.S.A.) was connected to three eluent reservoirs, A, B and C. In this arrangement, solvent A could be switched to B or C by manipulating the solvent selector valve without perturbing the pressure at the pump outlet/column inlet. The pump outlet was connected to the column assembly, consisting of six columns in parallel, mounted in a thermostated bath (Model TX9 thermostat from Tamson, Zoetermeer, The Netherlands) between two Model 7060 six-way valves (Rheodyne, Cotati, CA, U.S.A.). The outlet of the column system was connected to a Model 401 differential refractometer detector of cell volume 10 μl (Waters Assoc.). The column temperature was measured as the temperature of the thermostating bath; the long-term stability was ±0.05 K. The flow-rate of the eluent was calculated from the time necessary to fill a calibrated glass tube, thermostated at 20.0 ± 0.1°C. The reproducibility of the flow measurement was ±0.005 ml/min; the long-term stability of the flow-rate was ±0.2%.

Experimental parameters

The mean column pressure, P_c, was calculated with the equation

$$P_c = P_i/2 \tag{12}$$

where P_i is the pressure at the column inlet. Typical values of P_c were 15–25 bar at a flow-rate of $\dot{V} = 1.0$ ml/min. The flow-rate, $\dot{V}$, was measured at the temperature (20.0°C) and pressure (atmospheric) of the flow meter. The retention times, t_R (= breakthrough times), were calculated from the integral average retention distances on the chart, determined by the graphical method described below. Retention volumes were calculated as

$$V_R = t_R \dot{V} \tag{13}$$

The eluent composition as a mass fraction was given by the method of preparation. The volume fraction was calculated by using the partial volume of the solute, which was calculated with eqn. 9.

Definition of the breakthrough volume, $V_R^*(su)$

When using CH_3O^2H and $C_2H_5O^2H$ as solutes, the exchange of surface protons for deuterons across the graft was never complete and depended on the time of the experiment. Therefore, for the determination of $V_R^*(su)$, every experiment was stopped after having pumped a volume of $V_{\mu/vNA}$ + 10.0 ml of the solution of the hydroxy-deuterated solute through the column, which displaced the solution of the unlabelled solute ($\varphi_{su} = \varphi_{su*}$). After this volume, the incoming concentration of the labelled solute, $\varphi_{su*}^{(in)}$ was not attained, as seen in Fig. 2 (typical values of $\varphi_{su*}^{(out)}$ were 93–96% of $\varphi_{su*}^{(in)}$). The amount of protons exchanged in this experiment is equivalent to the volume of labelled solute, calculated as the shadowed area in Fig. 2. The volume $V_R^{(0)}(su)$ was determined in a previous experiment as the breakthrough volume AN → su/AN. The evaluation was made as follows. First, the integral average retention volume, $V_R^*(su)$, was determined by a graphical evaluation. The exchange capacity, $V_{\kappa,exch}$, calculated with eqn. 2, is then equivalent to the shadowed area. Note that, by exchanging all surface protons during the experiment (this is the case when water is used as a solute), a limiting value of $V_R^*(su)$ would be attained. This limit is also shown in Fig. 2.

The average contact time of exchange was approximated as follows. In the actual experimental setup, the holdup volume, $V_{\mu/vNA}$, was the sum of a large holdup volume before the column, designated $V_\mu^{(pump)}$, and the effective holdup volume of the column, $V_{\mu/vNA}^{(col)}$ (typically around 2.3 ml).

$$V_{\mu/vNA} = V_\mu^{(pump)} + V_{\mu/vNA}^{(col)} \tag{14}$$

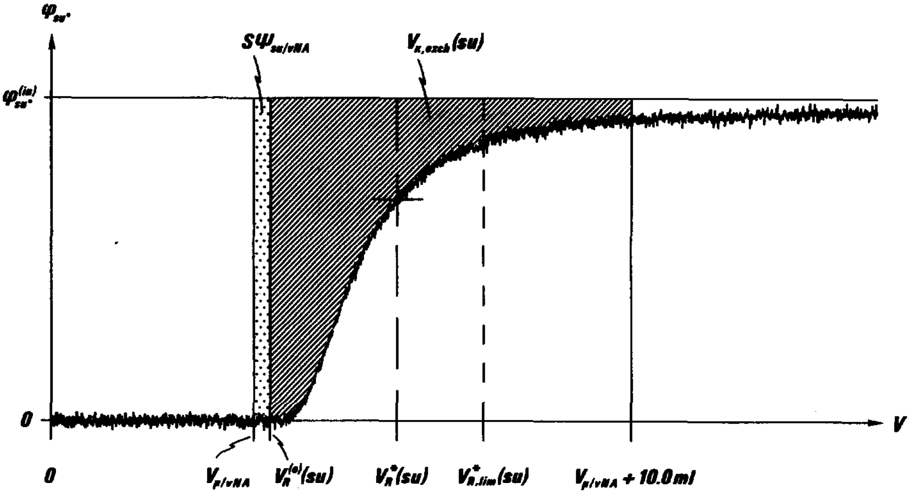


Fig. 2. Example of the graphical evaluation of a breakthrough experiment. Experimental conditions: displacement of a CH_3OH solution by CH_3O^2H solution; $T_c = 40.0°C$; $100\varphi_{su} = 100\varphi_{su*} = 0.99$; $\dot{V} = 1.89$ ml/min (see Table II). For a description of the evaluation, see text.

The experiment was conducted during the time t_{exp}:

$$t_{exp} = (V_{\mu/vNA} + 10.0)/\dot{V} \tag{15}$$

The inlet of the column was in contact with the labelled solute during the time $t_{exp} - t_{\mu}^{(pump)}$, but the effect of the exchange is observed in the detector only $t_{\mu/vNA}^{(col)} = V_{\mu/vNA}^{(col)}/\dot{V}$ later. The contact time at the end of the column with su* is $t_{exp} - t_R^*(su)$, and the effect of the exchange is seen immediately afterwards in the detector. Therefore, the average contact time of the adsorbent is approximately

$$\bar{t} = t_{exp} - \frac{1}{2}[t_{\mu/vNA} + t_R^*(su)] = \frac{1}{\dot{V}}\{10.0 - \frac{1}{2}[V_R^*(su) - V_{\mu/vNA}]\} \tag{16}$$

Experiments

In a first series of experiments, the breakthrough volumes, $V_R^{(0)}$ (AN → su/AN) and V_R^* (su/AN → su*/AN), were determined (su = methanol and ethanol) on the DMB-covered surface at constant eluent flow-rate ($\dot{V} \approx 1.9$ ml/min) and different temperatures, ranging from 20.0 to 80.0°C. The void volume, $V_{\mu/vNA}$, was also determined (breakthrough volume AN → AN*). The exchange capacity, $V_{\kappa,exch}$, was calculated with eqn. 2; the surface concentration of protons accessible for $H/^2H$ exchange was calculated with eqn. 3. For the experimental conditions and results, see Table II.

In a second series of experiments, the breakthrough volumes, $V_R^{(0)}$ and V_R^*, were measured on the DMB-covered adsorbent with methanol and ethanol as solutes at 20.0 ± 0.1°C and different eluent flow-rates, ranging from $\dot{V} = 1.9$ to 5.6 ml/min. For the results, see Table III.

TABLE II

SURFACE CONCENTRATION OF PROTONS ACCESSIBLE ACROSS THE DMB GRAFT FOR $H/^2H$ EXCHANGE FROM DILUTE SOLUTIONS OF METHANOL AND ETHANOL IN ACETONITRILE AS A FUNCTION OF TEMPERATURE

Experimental conditions: surface area of the adsorbent, $S = 346 \pm 4$ m^2 (for other characteristics of column A, see Table I); volume fraction of the unlabelled and labelled solute in acetonitrile, $100\varphi_{CH_3OH} = 100\varphi_{CH_3OH^*} = 0.992 \pm 0.002$ and $100\varphi_{C_2H_5OH} = 100\varphi_{C_2H_5OH^*} = 0.998 \pm 0.002$. T_c = Column temperature; $\dot{V}$ = flow-rate of the eluent at 20.0 ± 0.1°C and atmospheric pressure; $V_R^{(0)}$ = breakthrough volume of a solution of methanol or ethanol in acetonitrile for a column filled with pure acetonitrile, *i.e.*, AN → su/AN, V_R^* is that for su/AN → su*/AN; $V_{\kappa,exch}$ = exchange capacity, calculated with eqn. 2; $\bar{t}$ = average contact time, calculated with eqn. 16; $\Gamma_{OH,acc}$ = surface concentration of protons accessible for $H/^2H$ exchange, calculated with eqn. 3. Standard deviations are given in the bottom row.

su	T_c (°C)	$\dot{V}$ (ml/min)	$V_R^{(0)}$ (ml)	V_R^* (ml)	$V_{\kappa,exch}$ (µl)	$\bar{t}$ (min)	$\Gamma_{OH,acc}$ (µmol/m^2)
Methanol	20.0	1.912	5.51	8.03	25.0	4.48	1.81
	40.0	1.887	5.48	8.76	32.5	4.33	2.35
	60.0	1.910	5.44	9.27	38.0	4.15	2.75
	80.0	1.899	5.34	10.06	46.8	3.96	3.38
Ethanol	20.0	1.884	5.28	7.20	19.2	4.75	0.95
	40.0	1.881	5.28	8.07	27.8	4.53	1.38
	60.0	1.896	5.21	9.09	38.7	4.23	1.92
	80.0	1.885	5.15	10.69	55.3	3.83	2.74
S.D.	0.1	0.005	0.02	0.06	0.6	0.03	0.03

TABLE III

SURFACE CONCENTRATION OF PROTONS ACCESSIBLE ACROSS THE DMB GRAFT FOR $H/^2H$ EXCHANGE FROM DILUTE SOLUTIONS OF METHANOL AND ETHANOL IN ACETONITRILE AS A FUNCTION OF FLOW-RATE

T_c = 20.0 ± 0.1°C; other experimental conditions, column characteristics and symbols as in Table II

su	$\dot{V}$ (ml/min)	$V_R^{(0)}$ (ml)	V_R^* (ml)	$V_{\kappa,exch}$ (µl)	$\bar{t}$ (min)	$\Gamma_{OH,acc}$ (µmol/m^2)
Methanol	1.912	5.51	8.03	25.0	4.48	1.81
	2.786	5.49	7.57	20.6	3.15	1.49
	3.702	5.48	7.18	16.9	2.42	1.22
	4.568	5.53	7.09	15.5	1.97	1.12
	5.450	5.51	6.88	13.6	1.67	0.98
Ethanol	1.884	5.28	7.20	19.2	4.75	0.95
	2.765	5.30	6.85	15.5	3.30	0.77
	3.665	5.25	6.63	13.8	2.52	0.68
	4.647	5.27	6.43	11.6	2.01	0.57
	5.591	5.30	6.39	10.9	1.67	0.54
S.D.	0.005	0.02	0.06	0.6	0.03	0.03

TABLE IV

POINTS ON THE ADSORPTION ISOTHERM OF WATER, $\Psi_{\mathrm{W/vNA}}$, ON THE DMP · CN-COVERED ADSORBENT FROM DILUTE SOLUTIONS OF WATER IN ACETONITRILE AS A FUNCTION OF THE VOLUME FRACTION OF WATER, $100\varphi_{\mathrm{w}}$

For characteristics of the column DMP · CN/A, see Table I; for the symbol $V_{\mathrm{R}}^{(0)}$, see Table II. Results ± standard deviations.

$100\varphi_W$	$V_R^{(0)}$ (ml)	$\Psi_{W/vNA}$ (nl/m^2)
0.142 ± 0.002	7.50 ± 0.13	8.6 ± 0.5
0.280 ± 0.002	6.53 ± 0.07	9.6 ± 0.6
0.463 ± 0.002	6.07 ± 0.04	10.0 ± 0.6
0.922 ± 0.002	5.69 ± 0.02	10.3 ± 0.7

In a third series of experiments, the breakthrough volumes, $V_{\mathrm{R}}^{(0)}$, were measured on the DMP · CN-covered adsorbent with dilute solutions of water in acetonitrile at constant flow-rate ($\dot{V} \approx 1.9$ ml/min) and temperature ($T = 20.0$°C) but different water concentrations, ranging from $100\varphi_{\mathrm{W}} = 0.14$ to 0.92%. The void volume, $V_{\mu/\mathrm{vNA}}$, was also determined. Points on the adsorption isotherm, $\Psi_{\mathrm{su/vNA}}$, were calculated with eqn. 5. For the results, see Table IV.

. In a last series of experiments, the breakthrough volumes, $V_{\mathrm{R}}^{(0)}$, were measured with methanol and ethanol as solutes on all adsorbents listed in Table I at constant flow-rate ($\dot{V} \approx 1.9$ ml/min) and temperature ($T_{\mathrm{c}} = 20.0$°C) but different solute concentrations, ranging from $100\varphi_{\mathrm{su}} = 0.14$ to 1.95%. The void volumes, $V_{\mu/\mathrm{vNA}}$, were also determined. For the results, see Table V.

RESULTS AND DISCUSSION

Unreacted silanols under a triorganylsiloxy graft can be deuterated across the graft on contact with dilute solutions of hydroxy-deuterated solutes in organic solvents. There was a striking difference between deuteration with deuterium oxide solutions and that with solutions of hydroxy-deuterated methanol and ethanol. A complete isotopic exchange was achieved by using deuterium oxide at volume percentages $100\varphi_{\mathrm{W}} < 1.0$ in chromatographic experiments[1,2], whereas for methanol and ethanol solutions of the same concentration the exchange was only partial and depended on the flow-rate in the chromatographic column and on the temperature of the breakthrough experiment.

In a series of experiments, a constant volume of the solution of the hydroxy-deuterated alcohol was pumped at different flow-rates through a column packed with DMB-covered adsorbent. The amount of unreacted protons exchanged for deuterons was determined from the breakthrough signal, as explained under Experimental. The results are listed in Table III. Let us now assume that there are two sorts of unreacted silanols. One sort is in a sterically unhindered position and its protons exchange easily, at a rate that can be considered to be instantaneous in the breakthrough experiment. The surface concentration of these protons is identified with that of relatively free-standing silanols, $\Gamma_{\mathrm{OH,free}}$. A second sort of proton is found on sterically hindered silanols. These protons exchange slowly if the graft is in contact with the solution of the

TABLE V

POINTS ON THE ADSORPTION ISOTHERM OF THE SOLUTES METHANOL AND ETHANOL, $\Psi_{\mathrm{su/vNA}}$, ON ADSORBENTS LISTED IN TABLE I, FROM DILUTE ACETONITRILE SOLUTIONS AS A FUNCTION OF THE VOLUME FRACTION OF THE SOLUTE, $100\varphi_{\mathrm{su}}$

$T_c = 20.0 \pm 0.1$°C; $\dot{V} \approx 1.9$ ml/min. For the meaning of $V_R^{(0)}$, see Table II. Standard deviations: S.D. $(100\varphi_{\mathrm{su}}) = 0.002$; S.D. $[V_R^{(0)}] = 0.02$ ml; the values of S.D. $(\Psi_{\mathrm{su/vNA}})$ given in the table are valid for all series at similar compositions.

Graft	*su = methanol*			*su = ethanol*		
	$100\varphi_{su}$	*$V_R^{(0)}$ (ml)*	*$\Psi_{su/vNA}$ (nl/m²)*	*$100\varphi_{su}$*	*$V_R^{(0)}$ (ml)*	*$\Psi_{su/vNA}$ (nl/m²)*
DMB	*Column B:*			*Column B:*		
	0.137	6.01	2.6	0.149	5.68	1.4 ± 0.1
	0.286	5.90	4.5	0.297	5.58	1.8 ± 0.2
	0.492	5.82	6.5	0.493	5.56	2.8 ± 0.4
	0.977	5.77	11.5	0.984	5.55	5.2 ± 0.8
	1.458	5.72	15.1	1.469	5.52	6.5 ± 1.2
	1.933	5.67	17.1	1.947	5.52	8.6 ± 1.6
DMP · CN	*Column B:*			*Column A:*		
	0.137	5.87	2.5	0.149	5.56	1.1
	0.286	5.75	4.3	0.297	5.53	2.0
	0.492	5.70	6.7	0.493	5.50	3.0
	0.977	5.63	11.5	0.984	5.46	4.8
	1.458	5.58	15.1	1.469	5.46	7.2
	1.933	5.55	18.5	1.947	5.44	8.5
C · 14	*Column A:*			*Column B:*		
	0.137	5.69	2.6	0.149	5.44	1.3
	0.286	5.53	4.2	0.297	5.40	2.2
	0.492	5.50	6.8	0.493	5.35	3.0
	0.977	5.44	11.8	0.984	5.32	5.1
	1.458	5.38	15.0	1.469	5.30	6.8
	1.933	5.34	17.7	1.947	5.27	6.3

protic solute. The surface concentration of such silanols is designated $\Gamma_{\mathrm{OH,hin}}$. The sum of the concentration of these protons is obviously equal to that of the unreacted silanols under the graft:

$$\Gamma_{\mathrm{OH,free}} + \Gamma_{\mathrm{OH,hin}} = \Gamma_{\mathrm{OH,u}} \tag{17}$$

If such a grafted adsorbent were in contact with an infinite volume of a solution of the deuterated solute and if all sterically hindered protons exchanged with the same first-order rate, the time dependence of the surface concentration of protons exchanged in this experiment would be given by

$$\Gamma_{\mathrm{OH,acc}} = \Gamma_{\mathrm{OH,free}} + \Gamma_{\mathrm{OH,hin}}(1 - \mathrm{e}^{-kt}) \tag{18}$$

where k is the rate constant and t is the contact time. By plotting the logarithm of the non-deuterated fraction of the surface protons, $\ln[(\Gamma_{OH,u} - \Gamma_{OH,acc})/\Gamma_{OH,u}]$, as a function of the contact time, t, the linear plot obtained permits the determination of the constants in eqn. 18. In our breakthrough experiments, the restricted volume of the mobile phase can certainly not be considered as an infinite deuteron reservoir. Also, the real contact time is unknown. The average contact time, $\bar{t}$, calculated with eqn. 16 (see Experimental) is believed to be proportional to the true contact time. Fig. 3 shows the logarithmic plot of the non-deuterated fraction of the surface silanols as a function of the average contact time, $\bar{t}$, after the adsorbent in the column was in contact with a standard amount of hydroxy-labelled alcohol solution. The concentration of unreacted silanols of $\Gamma_{OH,u} = 4.54$ μmol/m^2 was calculated with $\Gamma_{DMB} = 3.90$ μmol/m^2 in eqn. 1. From the resulting linear plot, an apparent rate constant, $k_{app}^{(20)}$, could be calculated, valid under the given experimental conditions (20°C, $100\varphi_{su} = 1.0\%$). This is believed to be parallel to the real rate constant. The apparent rate constants and the corresponding time necessary to deuterate the surface to an extent of 50% $[t_{1/2}^{(20)} = \ln 2/k_{app}^{(20)}]$ are listed in Table VI. The dependence of the rate constant on the concentration of the contacting solution was not examined. Therefore, k_{app} is only defined for the specific concentration used in these experiments. It is probable that the

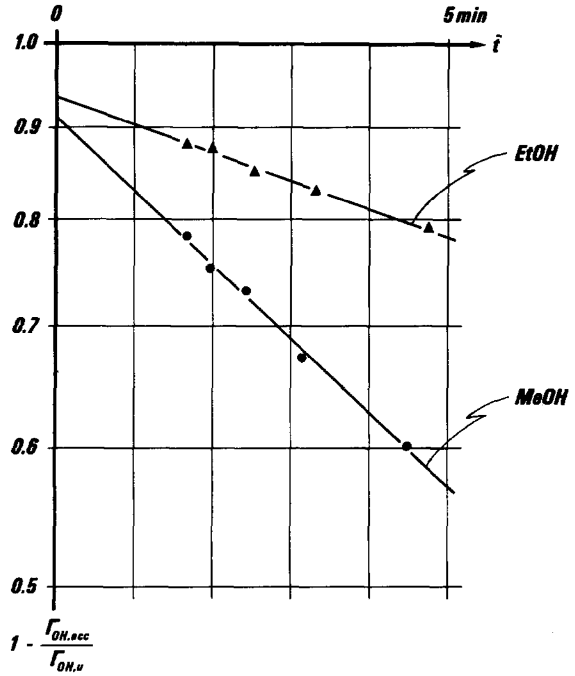


Fig. 3. Logarithmic plot of the molar fraction of the non-deuterated part of the unreacted silanols under the graft after contact with a standard amount of a dilute solution of the deuterated solute, CH_3O^2H and $C_2H_5O^2H$ ($\varphi_{su} = \varphi_{su*} = 0.010$) as a function of the average contact time, $\bar{t}$. The latter was calculated from the flow-rate with eqn. 16 (see Table III). EtOH = Ethanol; MeOH = methanol.

TABLE VI

SURFACE CONCENTRATION OF FREE-STANDING AND STERICALLY HINDERED SILANOLS, $\Gamma_{OH,free}$ AND $\Gamma_{OH,hin}$, ON DMB-COVERED SILICA, AS MEASURED BY H/^{2}H EXCHANGE

Data for water are from ref. 2. Also given are the apparent rate constants, $k_{app}^{(20)}$, and the corresponding half-life, $t_{1/2}^{(20)}$, of the exchange of the protons of the hindered silanols (under the experimental conditions T_c = 20°C and $100\varphi_{su} = 1.0$; see Table III). The activation energies of the latter exchange, $\Delta E^{\dagger}$, were calculated from data between 20 and 80°C (see Table II). Estimated errors (± values) are 95% confidence limits.

Solute	$\Gamma_{OH,free}$ *(μmol/m²)*	$\Gamma_{OH,hin}$ *(μmol/m²)*	$k_{app}^{(20)}$ *(min⁻¹)*	$t_{1/2}^{(20)}$ *(min)*	$\Delta E^{\dagger}$ *(kcal/mol)*
Water	4.54 ± 0.10	0.0	–	–	–
Methanol	0.39 ± 0.16	4.15 ± 0.14	0.094 ± 0.013	7.3 ± 1.1	4.1 ± 0.4
Ethanol	0.30 ± 0.12	4.24 ± 0.06	0.036 ± 0.006	19.5 ± 3.8	6.3 ± 0.6

exchange rate is not linearly proportional to the bulk concentration but to that of the concentration of the solute in the physically adsorbed layer at the graft–solution interface. Therefore, the slower exchange with ethanol as solute might be partly due to its lower molar concentration at $100\varphi_{su} = 1.0$ compared with methanol.

Extrapolation of the logarithmic plot in Fig. 3 to $\bar{t} = 0$ (infinite flow-rate) gives the relative concentration of protons that do not exchange at a very short contact time, *i.e.*, the fraction of the hindered silanols $\Gamma_{OH,hin}/\Gamma_{OH,u}$. It is seen that this fraction constitutes the main part and that it is different for methanol and ethanol, being 91 and 94%, respectively. The corresponding remainder is the proportion of the "free-standing" silanols. In fact, if these silanols were really unhindered, their concentration should not depend on the size of the deuterating solute.

For the evaluation of the deuteration experiments at different temperatures it was assumed that the surface concentration of the "free silanols" seen by the individual solutes did not depend on temperature. The extent of deuteration by a constant amount of solution at one (about constant) flow-rate is listed in Table II. A knowledge of the surface concentration of $\Gamma_{OH,free}$ now allowed us to calculate apparent rate constants. These are plotted in Fig. 4 on a logarithmic scale as a function of the inverse of the absolute temperature. From the slope of the plot, an activation energy of $\Delta E^{\dagger}$ = 4.1 and 6.3 kcal/mol was calculated for the deuteration across the graft with solutions of deuterated methanol and ethanol, respectively (see Table VI).

On the basis of these results, we conclude that the access to all unreacted silanols is sterically hindered by the dense graft. Also, there is no reason to postulate the presence of two sorts of silanols, free and hindered, as stated for the model which gave the starting picture for the evaluation of the kinetic results. Rather, it is probable that all the silanols are hindered but to different extents, and the apparent deuteration rates and activation energies are properties of an average silanol. The amplitude of the observed activation energy is of an order which might correspond to "making a hole" in the dense graft. By the vibrational motion of the substituents, access to a silanol is occasionally open. Consequently, almost every silanol is free at a certain but differing proportion of time.

In Fig. 5 are shown adsorption isotherms of methanol and ethanol from

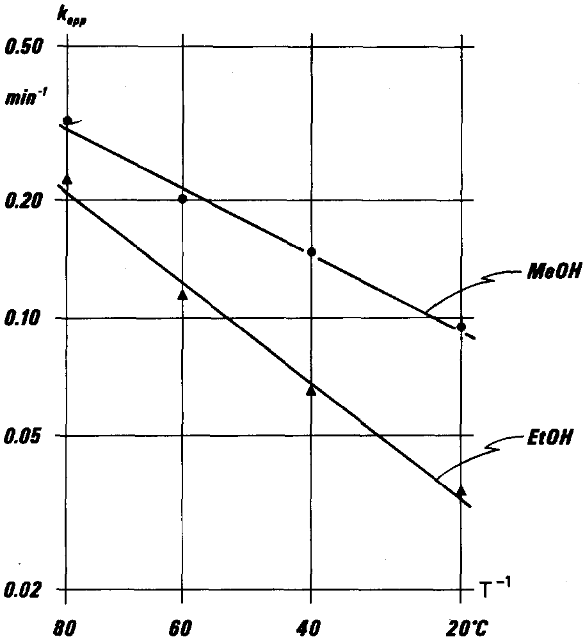


Fig. 4. Logarithmic plot of the apparent deuteration rate of the sterically hindered silanols as a function of the reciprocal of the absolute temperature. Rate constants were calculated from results in Table II.

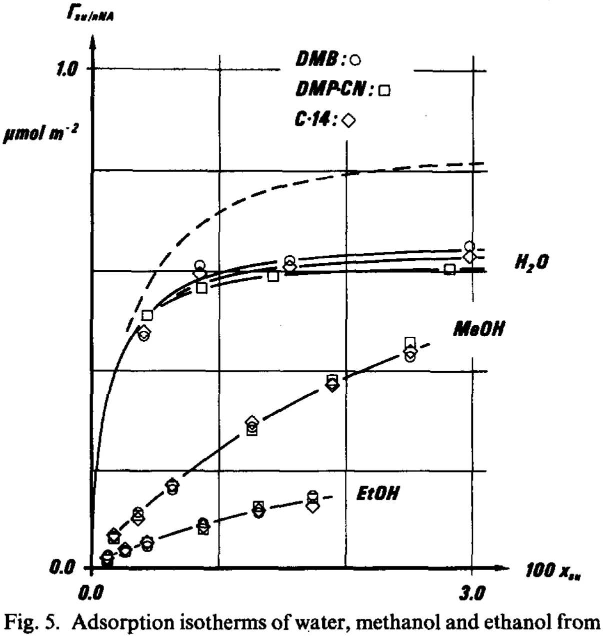


Fig. 5. Adsorption isotherms of water, methanol and ethanol from dilute solutions in acetonitrile on dense grafts of DMB, DMP · CN and C · 14 substituents on silica at 20.0°C. Isotherms, $\Gamma_{su/nNA}$, in units of μmol/m^2 were calculated from the isotherms $\Psi_{su/vNA}$ determined in units of μl/m^2. Traces of the water isotherm were calculated from the Everett–Klinkenberg representation of the adsorption and traces of the methanol and ethanol isotherms were drawn by eye. The broken line is the trace of the water adsorption isotherm on a DMP · CN graft 92% of the maximum density from ref. 2.

acetonitrile solutions at low concentrations in units of μmol/m². The conversion of the isotherms, determined as $\Psi_{\mathrm{su/vNA}}$ in units of μl/m², was effected using eqn. 9 in ref. 2:

$$\Gamma_{\mathrm{su/nNA}} = \Psi_{\mathrm{su/vNA}} \cdot \frac{1}{v_\mu} \cdot \frac{x_{\mathrm{su}} x_{\mathrm{AN}}}{\varphi_{\mathrm{su}} \varphi_{\mathrm{AN}}} \tag{19}$$

where v_μ is the molar volume of the mixture of mole fraction x_{su}. For the sake of consistency, the isotherm Γ_{su} is referred to the nNA Gibbs convention "*N*othing is *A*dsorbed in terms of *n*umber of moles", defined by the equation

$$\Gamma_{\mathrm{su}} + \Gamma_{\mathrm{AN}} = 0 \tag{20}$$

The adsorption isotherms of water on the DMB- and C · 14-grafted silicas were taken from ref. 2. The broken line shows the trace of the description of the adsorption isotherm by the Everett–Klinkenberg equation on a DMP · CN-covered sample, where the graft was only 92% of the maximum density. The adsorption isotherm of water on a dense DMP · CN graft was determined in this work (see Tables V and VII). It is now of interest that the isotherms of different but dense grafts are very similar. For the description of the water isotherms, the following picture may be given. About 0.7 μmol/m² of the silanols appear as active sites for water adsorption; the sites are all occupied at water concentrations as low as $100\varphi_{\mathrm{W}} \approx 0.3\%$. For the estimation of the molar surface concentration of the sites it was assumed that one site accommodates one water molecule. The adsorption isotherms of water on dense and loose DMP · CN grafts support this hypothesis. In fact, on the less dense graft (0.3 μmol/m²), an additional amount of 0.3 μmol/m² of water is adsorbed at saturation.

The shape of the methanol and ethanol adsorption isotherms differs fundamentally from that of water. Because the excess adsorption is positive, it is probably that the presence of the unreacted silanols does contribute to the adsorption of the alcohols, but certainly to a lesser extent. In fact, if there were silanols without steric hindrance where the alcohols are retained by hydrogen bonds, the alcohol isotherms would be similar to that of water, *i.e.*, of the Everett–Klinkenberg type with saturation of active sites at low solute concentrations. Therefore, it can be concluded that the

TABLE VII

CONSTANTS OF THE EVERETT–KLINKENBERG EQUATION, *b* AND *c* (EQN. 6), FOR THE DESCRIPTION OF THE WATER ADSORPTION ISOTHERM, $\Psi_{\mathrm{W/vNA}}$, FROM ACETONITRILE AT LOW VOLUME FRACTIONS ($100\varphi_{\mathrm{W}} < 1.0$) ON DMP · CN-COVERED SILICAS

Data for the adsorbent covered with a loose DMP · CN-layer are from ref. 2 and those on the surface covered with a dense layer were calculated from data given in Table IV. The symbol $\Psi_{\mathrm{Siol}} = 1/c$ is for the limiting surface concentration of water retained on specific adsorption sites; Γ_{Siol} is its molar equivalent. Errors (± values) are 95% confidence limits.

Layer	Γ_{sox} (μmol/m²)	*b* (m²/μl)	*c* (m²/μl)	Ψ_{Siol} (nl/m²)	Γ_{Siol} (μmol/m²)
Loose	3.66 ± 0.04	0.057 ± 0.009	65 ± 10	15.4 ± 2.6	0.91 ± 0.14
Dense	3.96 ± 0.04	0.034 ± 0.004	92 ± 11	10.8 ± 1.3	0.64 ± 0.08

so-called "silanol effect" in the adsorption at the surface of grafted silicas shows a pronounced dependence on the steric environment of the proton donor/acceptor group of the adsorbate. For the adsorption of solutes from water–organic solvent mixtures, the situation might be slightly different. In fact, in these ternary systems, the water saturates the specific sites and displaces the solute molecules.

ACKNOWLEDGEMENT

This paper is part of a project supported by the Fonds National Suisse de la Recherche Scientifique.

REFERENCES

1 J. Goworek, F. Nooitgedacht, M. Rijkhof and H. Poppe, *J. Chromatogr.*, 352 (1986) 399.
2 G. Fóti and E. sz. Kováts, *Langmuir*, (1989) in press.
3 F. Riedo and E. sz. Kováts, *J. Chromatogr.*, 239 (1982) 1.
4 R. K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979.
5 N. L. Ha, J. Ungvárai and E. sz. Kováts, *Anal. Chem.*, 54 (1982) 2410.
6 F. Köster, *Doctoral Thesis*, Ruhr-Universität Bochum, Bochum, 1984.
7 C. S. Koch, F. Köster and G. H. Findenegg, *J. Chromatogr.*, 406 (1987) 257.
8 D. H. Everett, *Trans. Faraday Soc.*, 60 (1964) 1803.
9 A. Klinkenberg, *Recl. Trav. Chim. Pays-Bas*, 78 (1959) 83.
10 G. Körösi and E. sz. Kováts, *Colloids Surfaces*, 2 (1981) 315.
11 D. Morel, J. Serpinet, J. M. Letoffe and P. Claudey, *Chromatographia*, 22 (1986) 103.
12 K. Szabó, N. L. Ha, Ph. Schneider, P. Zeltner and E. sz. Kováts, *Helv. Chim. Acta*, 67 (1984) 2128.
13 K. D. Lork, K. K. Unger and G. N. Kinkel, *J. Chromatogr.*, 352 (1986) 199.
14 D. Amati and E. sz. Kováts, *Langmuir*, 3 (1987) 687.
15 N. L. Ha and E. sz. Kováts, *Chromatographia*, 15 (1982) 61.
16 J. Gobet and E. sz. Kováts, *Adsorpt. Sci. Technol.*, 1 (1984) 285.
17 J. Gobet and E. sz. Kováts, *Adsorpt. Sci. Technol.*, 1 (1984) 77.
18 G. Fóti, M. L. Belvito and E. sz. Kováts, *J. Chromatogr.*, 440 (1988) 315.
19 D. Amati and E. sz. Kováts, *Langmuir*, 4 (1988) 329.