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## **Diffusion of sorbed pyrene in the bonded layer of reversed-phase silicas**

### **Effect of alkyl chain length and pore diameter**

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#### **ABSTRACT**

The processes of lateral diffusion of solutes in the bonded layer of *n*-alkylchlorosilane-modified silicas were studied using pyrene as a luminescence probe. It was shown that all bonded-chain carbon atoms interact with the solute for supports of pore diameter 40–50 nm. The reduction of the average pore diameter results in partial permeation of the solute into the bonded layer, which in turn leads to a decrease in apparent viscosity of the bonded layer. The presence of accessible silanol groups causes a strong decrease in pyrene mobility in the bonded layer.

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#### **INTRODUCTION**

The most informative method for the investigation of the state and dynamics of surface-adsorbed molecules is high-sensitivity luminescence. This method considers the diffusion-limited processes of probe molecules: luminescence quenching, non-radiating energy transfer of electronic excitation and formation of exciplexes (excited complexes) and excimers (excited dimers) [1–5].

The most successfully applied luminescence probe material is pyrene: it provides quantitative data on diffusion of adsorbed molecules [6–8] and allows study of conformational organization of the bonded layer of reversed-phase packings in liquid chromatography [9–11]. Knowledge of the dynamic behaviour of molecules adsorbed in the bonded layer allows prediction of the properties of reversed-phase packings and more understanding of their chromatographic non-reproducibility.

This paper deals with the study of pyrene lateral diffusion in the bonded layer of *n*-alkylsilane-modified silicas. Emphasis is placed on the effect of the bonded alkyl chain length and average pore diameter.

## EXPERIMENTAL

### *Silica supports*

The relevant characteristics of the silica supports used in this work are given in Table I. The specific surface area was determined by benzene adsorption [13].

### *Modification of silica surfaces*

Modification was carried out using absolute octane as solvent and absolute pyridine as activator [14].

### *Additional silanization (end-capping)*

Silanization was effected with a trimethylchlorosilane-hexamethyldisilazane (1:2) mixture.

### *Surface concentration of bonded alkyl groups*

The surface concentration of bonded alkyl groups was determined through carbon content analysis and eqn. 1 [14]:

$$P \text{ (}\mu\text{mol/m}^2\text{)} = \frac{10^6 P_c}{(1200n_c - P_c M)S} \quad (1)$$

TABLE I  
CHARACTERISTICS OF THE MODIFIED SILICAS

Sample	Initial support			Modifier	Carbon content (%)	Bonding density ( $\mu\text{mol/m}^2$ )	Sample symbol <sup>a</sup>
	Type	Specific surface area ( $\text{m}^2/\text{g}$ )	Pore diameter (nm)				
1	Silochrom C-80	67	45	$\text{ClSi}(\text{CH}_3)_3$	1.1	4.0	$\text{MC}_1$
2	Silochrom C-80	67	45	$\text{ClSi}(\text{CH}_3)_2\text{C}_6\text{H}_{13}$	2.3	4.0	$\text{MC}_6$
3	Silochrom C-80	67	45	$\text{Cl}_3\text{SiC}_8\text{H}_{17}$	2.0	2.7	$\text{TC}_{8/S}$
4	Silochrom C-80	67	45	$\text{Cl}_3\text{SiC}_8\text{H}_{17}$	1.9	2.7	$\text{TC}_8$
5	Silochrom C-80	67	45	$\text{Cl}_3\text{SiC}_{12}\text{H}_{25}$	4.0	3.67	$\text{TC}_{12/S}$
6	Silochrom C-80	67	45	$\text{Cl}_3\text{SiC}_{16}\text{H}_{33}$	5.3	3.67	$\text{TC}_{16/S}$
7	Silochrom C-80	67	45	$\text{Cl}_3\text{SiC}_{16}\text{H}_{33}$	5.1	3.67	$\text{TC}_{16}$
8	Silochrom C-80	67	45	$\text{Cl}_3\text{SiC}_{18}\text{H}_{37}$	5.7	3.67	$\text{TC}_{18/S}$
9	A-300	166	25	$\text{ClSi}(\text{CH}_3)_2\text{C}_{16}\text{H}_{33}$	10.3	3.33	$\text{MC}_{16}$
10	KCK-2	186	13.5	$\text{ClSi}(\text{CH}_3)_2\text{C}_{16}\text{H}_{33}$	11.4	3.33	$\text{MC}_{16}$
11	Si-100	283	11.5	$\text{ClSi}(\text{CH}_3)_2\text{C}_{16}\text{H}_{33}$	15.3	3.16	$\text{MC}_{16}$
12	Si-60	476	5.4	$\text{ClSi}(\text{CH}_3)_2\text{C}_{16}\text{H}_{33}$	17.6	2.21	$\text{MC}_{16}$

<sup>a</sup> S = Sample end-capped by trimethylchlorosilane-hexamethyldisilazane; M, T = treatment with mono- and trichlorosilanes, respectively.

where  $P$  is the surface concentration of the bonded alkyl group,  $n_c$  is the number of carbon atoms in the modifier molecule,  $M$  is the corrected molecular weight of organosilicon modifier,  $P_c$  is the carbon content (%) of the sample and  $S$  is the specific surface area of initial silica. The surface concentrations of the bonded alkyl groups for synthesized silicas are listed in Table I.

#### *Introduction of pyrene onto the support surface*

Pyrene was introduced from a solution in hexane; this was then followed by solvent removal *in vacuo* (10 Torr) at 35–40°C for 15–20 min. For wide-pore modified silicas (samples 1–8, Table I), the surface concentration of pyrene was determined from eqn. 9 (see below) and varied between  $8.3 \cdot 10^{-4}$  and  $0.16 \mu\text{mol}/\text{m}^2$ . This range corresponds to 0.1–20% of surface monolayer coverage given a pyrene adsorption area on silica of  $1.5 \text{ nm}^2$  [4].

For narrow-pore modified silicas (samples 9–12, Table I), the surface concentration of pyrene was determined from eqns. 10 and 11 and varied between  $2.2 \cdot 10^{-3}$  and  $0.20 \mu\text{mol}/\text{m}^2$ .

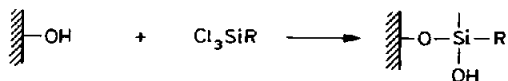
#### *Fluorescence excitation and fluorescence spectra*

Fluorescence was measured with a Perkin-Elmer LS-5 spectrofluorimeter; solid samples in cuvettes (2.5-nm bandpass).

### RESULTS AND DISCUSSION

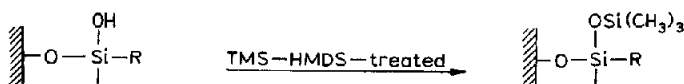
The synthesized adsorbents may be classified into three types on the basis of their potential interaction with pyrene:

(I) Samples obtained by modification with alkyltrichlorosilanes ( $\text{RSiCl}_3$ ). The interaction of such modifiers with the silica surface affords the following structure [14,15]:

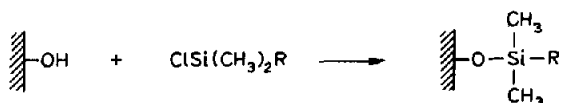


Consequently, a significant amount of accessible silanol groups is present on the sample surface [14,15].

(II) Samples prepared by modification with alkyltrichlorosilanes and additionally silanized (end-capped) by a trimethylchlorosilane (TMS)–hexamethyldisilazane (HMDS) mixture. Such treatment leads to shielding of residual silanol groups [14,15]:



(III) Samples treated with alkyldimethylchlorosilanes of the general formula  $\text{ClSi}(\text{CH}_3)_2\text{R}$ . After such treatment residual silanol groups on the surface are mainly shielded [14,15]:



It would be expected that adsorbents having shielded residual silanol groups (types II and III) will show weak adsorbate-adsorbent dispersion interactions (Fig. 1a). Increasing the bonded alkyl chain length may intensify these interactions due to pyrene dissolution in the bonded hydrocarbon layer.

For adsorbents with accessible silanol groups (type I) specific interaction of pyrene with silanol groups is possible (Fig. 1b).

Reduction of the silica support average pore diameter leads to the formation of a "conformationally rigid" bonded layer structure [16] which should also affect the behaviour of adsorbed molecules (Fig. 1c).

*Formation of pyrene excimers on the support surface. Calculation of the coefficient of lateral diffusion*

*Effect of alkyl chain length and end-capping.* The excitation fluorescence and fluorescence spectra of the various wide-pore silica samples (samples 1-8, Table I) were measured over a wide range of pyrene concentration.

Electronic-vibration bands typical of pyrene monomer were observed in fluorescence excitation and fluorescence spectra at low degrees of surface coverage (Fig. 2). The increase of pyrene surface concentration results in fluorescence of excimers, as has been found for solutions [17,18], with a maximum at 460 nm. However, the excitation fluorescence spectra coincides with that of pyrene monomer (Fig. 3).

Excimer formation depends on both bonded alkyl chain length and the presence of accessible silanol groups. The minimum concentration required for supports of types II and III for formation of pyrene excimers increases with increasing bonded alkyl chain length (Table II). The formation of pyrene excimers was not observed on silicas with accessible surface silanol groups (Type I) at up to 20% pyrene monolayer surface coverage (Table II, last two lines).

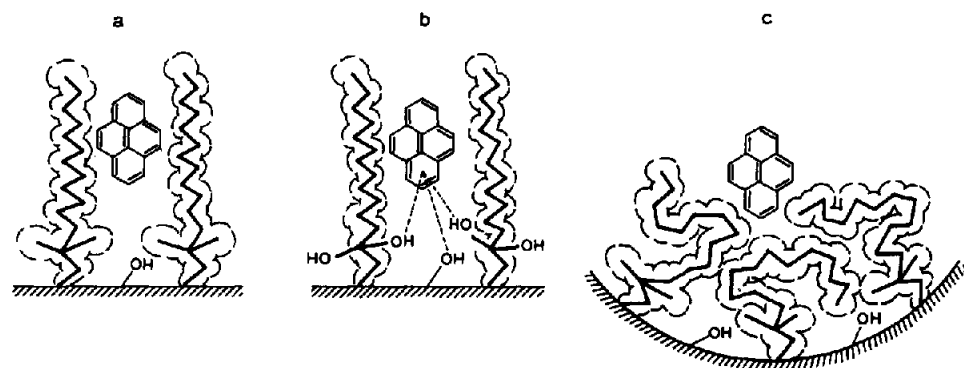


Fig. 1. Interaction of pyrene with the bonded layer of modified silicas.

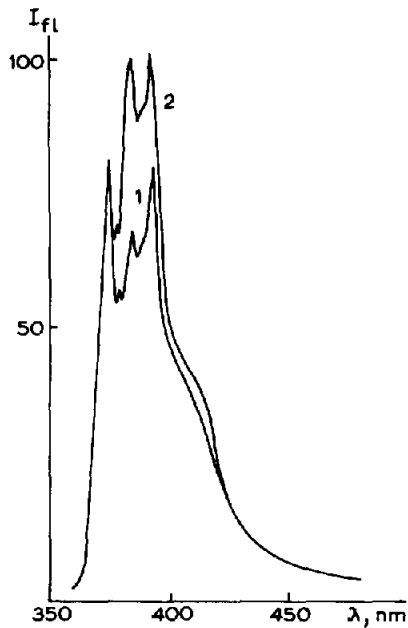


Fig. 2. Normalized fluorescence spectra of pyrene sorbed on (1) octyltrichlorosilane-modified silica and (2) the same sample after end-capping. Surface concentration of pyrene in both cases:  $2.5 \cdot 10^{-2} \mu\text{mol}/\text{m}^2$ .

The surface formation of pyrene excimers is a diffusion-limited process. A qualitative description of the observed effects can be obtained using the Einstein-Smolukhovsky equation:

$$D = \langle \Delta x \rangle^2 / 4t \quad (2)$$

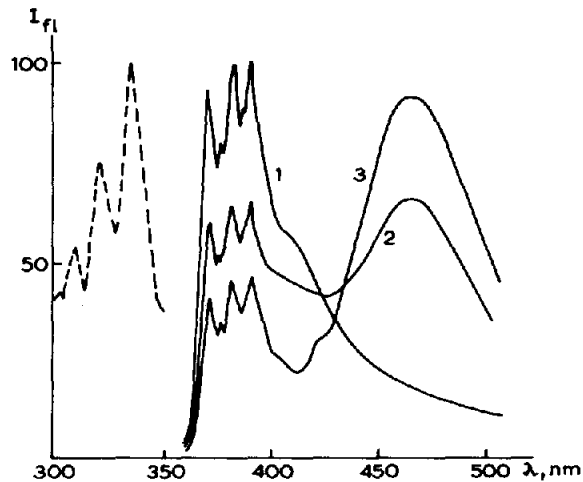


Fig. 3. Normalized excitation (broken line) and emission (solid line) fluorescence spectra of pyrene sorbed on hexyldimethylchlorosilane-modified silica. Surface concentration of pyrene: 1 =  $0.83 \cdot 10^{-3}$ ; 2 =  $4.20 \cdot 10^{-3}$ ; 3 =  $8.30 \cdot 10^{-3} \mu\text{mol}/\text{m}^2$ .

TABLE II

## STATE OF PYRENE IN THE BONDED LAYER OF ALKYL-SILANE-MODIFIED SILICAS

M = Monomer; E = excimer; P = phase. Support C-80.

Sample <sup>a</sup>	Surface concentration of pyrene ( $\mu\text{mol}/\text{m}^2 \cdot 10^3$ )										
	0.83	2.5	4.4	4.2	5.0	8.3	16	25	33	130	160
MC <sub>1</sub>	E	E	E	E	E	P	P	P	P	—	—
MC <sub>6</sub>	M	M	E	E	E	E	E	P	P	P	—
TC <sub>8/S</sub>	M	M	E	E	E	E	E	E	P	P	—
TC <sub>12/S</sub>	M	M	M	M	M	M	M	E	E	P	P
TC <sub>16/S</sub>	M	M	M	M	M	M	M	M	E	E	E
TC <sub>18/S</sub>	M	M	M	M	M	M	M	M	M	E	E
TC <sub>8</sub>	M	M	M	M	M	M	M	M	M	M	M
TC <sub>16</sub>	M	M	M	M	M	M	M	M	M	M	M

<sup>a</sup> Notations as in Table I.

where  $D$  is the diffusion coefficient, and  $\Delta x$  and  $t$  are the length and time of the molecule jump, respectively. Considering  $t$  as the lifetime of the pyrene monomer in an excited state (680 ns [18]) and  $\Delta x$  as the mean distance between pyrene molecules ( $l$ ), given by the equation  $l = 1.075/\sqrt{C_0}$ , where  $C_0$  is the surface pyrene concentration in molecules per  $\text{nm}^2$  at which the intensity of excimer fluorescence at 460 nm is three times the noise level, it is possible to estimate (using eqn. 2) the diffusion coefficient of pyrene in bonded layer of the modified silicas. The results are given in Table III.

Such an approach is only applicable for a qualitative description of diffusion in the bonded layer, as pyrene molecules may not be uniformly distributed on the surface,  $\Delta x \neq l$ , and  $t$  depends on the nature of the support.

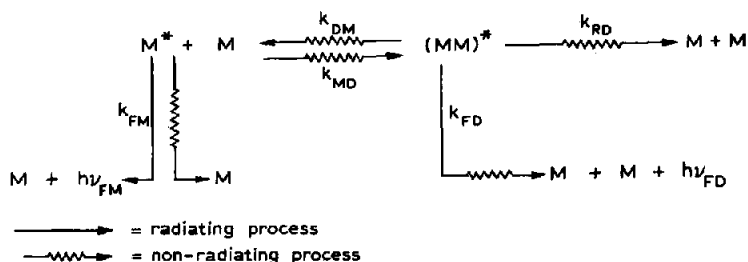
TABLE III

## PHYSICO-CHEMICAL CHARACTERISTICS OF LATERAL DIFFUSION PROCESSES OF PYRENE IN BONDED LAYER OF ALKYL-SILANE-MODIFIED SILICAS

Sample No.	Sample <sup>a</sup>	$n_C$ (atoms/ $\text{nm}^2$ )	$C_0 \cdot 10^3$ ( $\mu\text{mol}/\text{m}^2$ )	Diffusion coefficient $\cdot 10^6$ ( $\text{cm}^2/\text{s}$ ) according to		$\eta$ (cP)	$k_{DM} \cdot 10^{-12}$ ( $\text{m}^2/\text{mol} \cdot \text{s}$ )	$E_a$ (kJ/mol)
				Eqn. 2	Eqn. 5			
1	MC <sub>1</sub>	6.9	0.41	5.28	2.60	1.7	1941	2.59
2	MC <sub>6</sub>	17.6	0.82	2.64	0.72	6.2	540	6.60
3	TC <sub>8/S</sub>	13.5	1.16	1.88	0.44	10.2	327	5.05
5	TC <sub>12/S</sub>	26.4	5.25	0.20	0.06	76.6	43	9.90
6	TC <sub>16/S</sub>	33.6	8.20	0.18	0.03	162.5	21	12.62
8	TC <sub>18/S</sub>	38.1	9.16	0.12	0.02	231.7	14	14.33
13	C <sub>6</sub> H <sub>14</sub>					0.29		
14	C <sub>18</sub> H <sub>38</sub>					3.81		
15	Glycerol					1480		

<sup>a</sup> Notations as in Table I.

The diffusion coefficients can be more accurately determined if the kinetics of pyrene excimer formation are considered [19,20]:



M and M\* are pyrene monomers in ground and excited states, respectively, (MM)\* is an excimer, and the  $k$  values are the rate constant of the corresponding radiating and non-radiating processes. Solving the steady-state equation and introducing the total surface concentration of pyrene,  $C$ , enables the ratio of excimer,  $I_{FD}$ , and monomer,  $I_{FM}$ , fluorescence intensities to be expressed thus:

$$I_{FD}/I_{FM} = k_{FD}k_{DM}C/k_{FM}k_D \quad (3)$$

where  $k_D = k_{FD} + k_{RD}$ .

The literature values [21] of  $k_{FD}$  ( $1.3 \cdot 10^7 \text{ s}^{-1}$ ),  $k_{FM}$  ( $1.5 \cdot 10^6 \text{ s}^{-1}$ ) and  $k_D$  ( $7.1 \cdot 10^7 \text{ s}^{-1}$ ) are almost independent of the solvent nature and can be used to determine the bimolecular reaction rate constant of excimer formation,  $k_{DM}$ , on the basis of the relationship  $I_{460 \text{ nm}}/I_{393 \text{ nm}} = F(C)$  thus derived from eqn. 3. The application of Smolukhovsky equation for diffusion-limited bimolecular reactions

$$k_{DM} = 2\pi DN_A \quad (4)$$

where  $N_A$  is Avogadro's number, allows calculation of the diffusion coefficients of pyrene, and the viscosity of the bonded layer ( $\eta$ ) when combined with the Stokes-Einstein equation

$$D = kT/6\pi b\eta \quad (5)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature and  $b$  is the Stokes radius.

Diffusion coefficients calculated according to eqns. 2 and 5 are given in Table III. As expected, diffusion coefficient values decrease with increasing bonded alkyl chain length. This dependence is described by eqn. 6:

$$D = \text{constant} \cdot \exp(-0.13n) = \text{constant} \cdot \exp(-0.37n/RT) \quad (6)$$

where  $n$  is the number of carbon atoms per  $\text{nm}^2$  of surface and  $R$  is the universal gas constant. The diffusion coefficient can also be expressed thus:

$$D = \text{constant} \cdot \exp(-E_a/RT) \quad (7)$$

This indicates that the activation energy ( $E_a$ ) of diffusion in the bonded layer is linearly related to the number of carbon atoms on the surface and to the bonded alkyl chain length. Eqn. 8:

$$E_a = 0.13nRT = 0.37n \quad (8)$$

obtained from eqns. 6 and 7 allows the determination of the activation energy values for pyrene diffusion in the bonded layer of modified silicas; these are given in Table III.

The results given in Table III show that the bonded alkyl layers have markedly higher viscosities than the corresponding liquid alkanes. This is due to the reduction in the degree of freedom after alkyl chain fixation on the silica surface. The diffusion of sorbed molecules in the bonded layer of reversed-phase silicas corresponds to that in viscous fluids.

*Effect of the support pore structure.* Fadeev and Staroverov [16] showed that the conformation structure of bonded long chain alkyl layers depends on the support pore structure. Reduction in average support pore diameter produces a bonded layer of "rigid structure" in contrast to the "flexible structure" found in wide-pore modified silicas.

This section considers the effect of support pore diameter on the physico-chemical characteristics of pyrene diffusion in a bonded silica layer modified by hexadecyldimethylchlorosilane. The samples used are described in Table I.

A similar procedure is used for investigating pyrene diffusion on both bonded layer and wide-pore samples. Using eqns. 3–5, the rate constants of excimer formation diffusion coefficients and bonded-layer viscosity were determined; the results are given in Table IV.

The only difference between the procedures involves the determination of the surface concentration of pyrene. Thus for wide-pore silica samples (type C-80, Table I) the surface areas accessible to benzene (specific surface area measurement) and pyrene are practically the same. C-80 is an aerosilgel, synthesized from aerosil and subjected to hydrothermal treatment. This leads to silicas which have a surface fractal dimension close to 2 [24]. The surface concentration of pyrene for samples 1–8 (Table I) may be defined [22,24] as follows:

$$C = m_{\text{pyr}}/S_{\text{benz}} \quad (9)$$

TABLE IV

EFFECT OF AVERAGE SILICA SUPPORT PORE DIAMETER ON PHYSICO-CHEMICAL CHARACTERISTICS OF PYRENE DIFFUSION IN THE BONDED LAYER OF HEXADECYL-DIMETHYLCHLOROSILANE-MODIFIED SILICAS

Sample No.	Average pore diameter (nm)	Surface fractal dimension	$S_{\text{pyr}}/S_{\text{benz}}$	Diffusion coefficient (cm <sup>2</sup> /s) according to eqn. 4	$\eta$ (cP)	$k_{\text{DM}} \cdot 10^{-12}$ (m <sup>2</sup> /mol · s)	%R (share of rigid structure [16])
9	25	2.3	0.84	0.036	117.3	30.4	2
10	13.5	2.4	0.79	0.120	44.3	76.8	60
11	11.5	2.6	0.71	0.061	81.2	46.7	30
12	5.4	2.8	0.64	0.135	36.0	94.1	100



where  $m_{\text{pyr}}$  is the amount of sorbed pyrene and  $S_{\text{benz}}$  is the specific surface area as determined by benzene adsorption [22].

In the case of a narrow-pore support, part of the surface accessible to benzene is inaccessible to large pyrene molecules [22]:

$$S_{\text{pyr}}/S_{\text{benz}} = (\sigma_{\text{pyr}}/\sigma_{\text{benz}})^{(2-d)/2} \quad (10)$$

where  $\sigma_{\text{pyr}}$  and  $\sigma_{\text{benz}}$  are cross-sectional areas for pyrene (1.5 nm<sup>2</sup>) and benzene (0.49 nm<sup>2</sup>) [4,13] and  $d$  is the surface fractal dimension. The surface concentration of pyrene for samples 9–12 (Table I) has been determined according to

$$C = m_{\text{pyr}}/S_{\text{pyr}} \quad (11)$$

It was found [22–24] that in general pore diameter and  $d$  are related. For non-porous and wide-pore silica,  $d$  values are low (2.0–2.2.); whereas  $d$  values of narrow-pore silicas, *e.g.*, type Si-60, are high (2.8–3.0) and  $S_{\text{pyr}}/S_{\text{benz}}$  may be much less than 1 (Table IV). The  $d$  values for Si-60, Si-100, KCK-2 (as for Si-200) and A-300 (as for Si-250) silicas were taken from ref. 23.

The results show that the efficient viscosity of the bonded hexadecyl layer reduces as the average pore diameter of the silica support decreases. This may be explained through the concept of a “rigid structure” of the bonded layer [16]. The reduction in viscosity (or increase in diffusion coefficient) reflects the decrease in dispersion interaction of the pyrene-bonded layer. The “rigid structure” of the bonded layer—formed by tightly interwoven alkyl chains—does not permit adsorbed pyrene molecules to permeate completely into the bonded layer (Fig. 1c). The bonded layer is much less accessible than wide-pore samples with “flexible structures” which are totally permeable to solute molecules. The smaller the average support pore diameter, the greater the rigid structure and the greater the difference in diffusion parameters (Table IV).

From this point of view sample 10 (Table IV) is of interest. It has an asymmetric pore size distribution curve and a significant “tail” in the small-pore region—in contrast to the symmetric distribution curves of other supports. The rigid structure of sample 10 is higher than, for example, of sample 11 (Table IV) and only loses a monotonic order of decreasing bonded-layer viscosity with reduction of average support pore diameter.

Thus, the decrease in average pore diameter results in only partial permeation of pyrene in the bonded layer. A narrow-pore silica such as Si-60 is not able to interact with silanol groups in spite of a low bonding density (only 2.2  $\mu\text{mol}/\text{m}^2$ , Table I, sample 12). For a wide-pore sample (such as C-80), modified by hexadecyltrichlorosilane with a bonding density of 3.7  $\mu\text{mol}/\text{m}^2$  (sample 7, Table I), pyrene interacts with silanol groups, leading to a sharp decrease in its mobility and an absence of excimer formation (Table II). The same result was reported by Avnir *et al.* [7]. It was shown that a relatively low viscosity corresponds to a densely packed layer, in contrast to partially modified silicas with accessible silanol groups.

#### *Aggregation of pyrene on the surface of modified silicas*

Increasing the surface concentration of pyrene results in the formation of

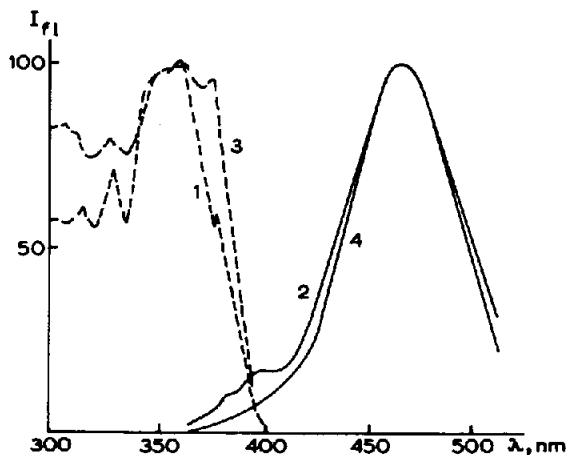


Fig. 4. Normalized excitation (broken line) and emission (solid line) fluorescence spectra of pyrene sorbed on silica modified by butyldimethylchlorosilane (1 and 2) and crystalline pyrene (3 and 4). Surface concentration of pyrene (1 and 2)  $1.60 \cdot 10^{-2} \mu\text{mol}/\text{m}^2$ .

a pyrene phase that is revealed as new bands in excitation and emission fluorescence spectra, typical of pyrene crystals (Fig. 4). This is unusual since the pyrene phase formation occurs at a very low degree of surface coverage (Table II). As a rule, formation of a phase on the surface is observed at close-to-monolayer coverage.

As with excimer formation, the minimum concentration required to produce this pyrene phase increase with increasing modifier chain length. In the case of samples modified by hexa- and octadecylsilanes, the formation of the phase was not observed even up to 20% surface coverage (Table II).

In our opinion, the formation of a pyrene phase on modified surfaces depends on the ratio of interaction energies between pyrene–pyrene and pyrene-bonded alkyl chains. For samples modified by short-chain silanes the formation of the phase is observed at 0.7–1.0% surface coverage. Increasing the bonded alkyl chain length leads to a growth in the dispersion interaction between pyrene and the bonded layer and thus to an increase in the minimum pyrene concentration at which the phase is formed (Table II).

Silicas treated with trichlorosilane without end-capping (type I) have increased surface–pyrene interaction energies due to specific interactions with accessible silanol groups (Fig. 1a). The presence of such interactions is confirmed by the change in vibrational structure of fluorescence spectra of pyrene adsorbed on the alkylchlorosilane-modified samples without end-capping in comparison with end-capped samples (Fig. 2). Interaction of pyrene with silanol groups results in a lack of pyrene phase formation, even at 20% surface monolayer coverage for a sample with bonded octyl groups (Table II, penultimate line).

## CONCLUSIONS

The experimental results presented here allow some general conclusions to be made about the dependence of the properties of silicas with bonded alkyl groups on chain length, pore diameter and accessibility of silanol groups.

Comparison of the samples with a large number of accessible silanol groups with the end-capped samples reveals the important role of silanol groups, which may exceed the role of the bonded alkyl chain length (Table II). The effect of the chain length and pore size on the character of solute bonded layer interaction can only be seen for samples with shielded silanol groups.

The linear relationship between activation energy of diffusion and the number of carbon atoms per unit of surface (eqn. 8) for wide-pore supports (pore diameter 40–50 nm) indicates that in this case all bonded carbon atoms participate in solute interaction.

For narrow-pore silicas, not all bonded alkyl chain atoms interact with the solute, as indicated by the decrease in apparent viscosity of the bonded layer. In case of the support with pore diameter 25 nm with bonded hexadecyl chains the bonded layer viscosity decreases 1.5 times comparing to the viscosity of the hexadecyl layer bonded to the support with pore diameter 45 nm. For supports with pore diameters *ca.* 10 nm or less the viscosity of the bonded layer corresponds to that of wide-pore samples with a bonded chain length of *ca.* 10–12 carbon atoms (Tables III and IV). In our opinion the results explain an observed [25] dependence of  $\log k'$  ( $k'$  = capacity factor) on the bonded chain length, which forms a plateau at the 12–14 carbon atoms chain length for supports with pore diameter 10–12 nm. For short bonded chains, pores of 10–12 nm are rather wide and all the bonded atoms interact with the sample molecule. Increasing the bonded chain length results in steric hindrance and only some of the bonded chain atoms participate in interaction.

It should also be mentioned that solute (pyrene) mobility within the bonded layer of hexadecyl groups varies with average pore diameter (Table IV). The chromatographic properties of even similar reversed-phase silicas should therefore be unlike due to the differences in their pore sizes. This is one reason for the discrepancy in properties between reversed-phase packings of various manufacturers and those obtained from various samples of the same silica.

Our results show that the most widely applied reversed-phase packings leave much to be desired. Further study is needed to optimize the modifier chain length and the structural and geometrical composition of the support. Problems with the reproducibility of reversed-phase packings should also be addressed.

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