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Phosphazenes on diatomaceous earths in water adsorption

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Hexachlorocyclotriphosphazene (T) and poly-bis-(trifluoroethoxy)phosphazene (A) deposited separately on wide-pore kieselguhr supports result in composite adsorbents of an increased adsorption capacity for water vapour per unit surface area. Deposition alters the adsorption behaviour of T and A themselves due to high dispersion and conformation changes of polymer chains within the pores in comparison with the initial solid state.

1. Introduction

Diatomaceous earths (kieselguhr) have found applications on an industrial scale as adsorbents, filters, fillers, catalyst supports etc. [1–3]. Chemical treatment of the raw material allows one to obtain products of high SiO_2 content and pores which have undergone a controllable redistribution in their size and shape [4, 5]. This would recommend diatomaceous earths as adsorbents supporting other substances, deposited in order to get composites of enhanced adsorption functionality.

In the present communication two phosphazenes are chosen to be the deposits, namely hexachlorocyclotriphosphazene (T) and linear poly-bis-(trifluoroethoxy) phosphazene (A). In spite of growing interest in phosphazene-based materials [6, 7], the adsorption properties of phosphazene compounds have been paid little attention so far. However, small rings like T and macromolecules like A can offer unconventional adsorption sites such as phosphorus and/or nitrogen atoms, not to speak of substituent effects and side groups. Interference with intrinsic adsorption sites of the support is also possible and the extent to which the overall adsorption behaviour would show additivity remains to be made clear.

Water is chosen to be the adsorptive substance because it is significant [8] in the chemistry of phosphazenes and less investigated with respect to adsorption on diatomaceous earths [5, 9, 10].

2. Experimental procedure

Three types of wide-pore kieselguhr support (Nos 1, 2, 3) have been used, Table I giving their characteristics. As seen, they differ in their thermal and chemical processing and, consequently, in porosity and surface chemistry. Note that No. 1 is a natural kieselguhr from the Dragovishtitsa deposit, Bulgaria, with a considerable amount of Al_2O_3, Fe_2O_3 and alkaline metal oxides, whereas Nos 2 and 3 are of a high SiO_2 content due to subsequent enrichment and/or chemical treatment of the diatomaceous earth rock.

On kieselguhr surfaces, as with silica gels, the part of adsorption sites for water molecules is played by Si atoms of broken coordination and OH groups. When raising the temperature at which diatomaceous raw material is processed (No. 1 < No. 2 < No. 3, Table I), the latter sites become less numerous as evidenced by i.r. spectra (curves 1, 2 and 3 in Fig. 1). Yet the admixtures. if not eliminated, should entail an additional spectrum of adsorption sites, acidic (Al^{3+}, Fe^{3+}, Na^+, K^+) as well as basic (O^{2-}). This may account for the fact that natural kieselguhr has an adsorption capacity for water vapour three to four times greater than that of wide-pore silica gels.

Phosphazene T, $(NPCl_2)_3$, was synthesized from PCl_5 and NH_4Cl dissolved in chlorobenzene at 138–140 °C following Lund *et al.* [11] and with a small amount of pyridine as catalyst. Upon steam distillation and two recrystallizations (light petroleum) crystals were obtained and identified by their melting point (112–114 °C), i.r. spectra, ^{31}P NMR spectra (showing an admixture of 0.5–1 wt % $(NPCl_2)_4$), X-ray diffraction (orthorhombic system) and elemental analyses.

Phosphazene A, $[NP(OCH_2CF_3)_2]_n$, was synthesized and characterized according to Korshak *et al.* in the Laboratory of Heterocyclic Polymers (Dr D. R. Tur) at the Nesmeyanov Institute of Elemento-organic Compounds, Moscow. It had a weight-average molecular mass (M_W) of 1.7×10^6, with X-ray fluorescence analysis recording 0.03 wt % Cl.

Deposition of phosphazenes T and A on support Nos 1, 2 and 3 proceeded in the following manner. The support was heated in air for 6 h at 105 °C, cooled down to room temperature and outgassed for 5 min at 2 torr. It was then allowed to imbibe drops of a phosphazene solution, the constant amount of which was chosen to ensure complete impregnation of the sample. The solvents were diethyl ether for T and

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TABLE I Characteristics of bare kieselguhr supports and individual phosphazenes

Sample	Symbol	Chemical composition	Surface area ($m^2 g^{-1}$)	Pore shape(s)	Pore size (nm)[b]	Total pore volume ($cm^3 g^{-1}$)
Kieselguhr support No. 1 (natural)	1	SiO_2 71 wt %, other oxides[a] 29 wt %	24	(a) Round cross-section cylinders, (b) bottle-necked	1.5×10^3	0.73
Kieselguhr support No. 2 (thermally and chemically treated at 650 °C)	2	SiO_2 93 wt %, other oxides[a] 7 wt %	40	(a) Round cross-section cylinders, (b) slit-like	1.5×10^3	1.32
Kieselguhr support No. 3 (thermally and chemically treated at 1000 °C)	3	SiO_2 88 wt %, other oxides[a] 12 wt %	0.8	Slit-like	6.5×10^3	1.06
Hexachlorocyclotriphosphazene	T	$(NPCl_2)_3$	< 0.01	–	–	–
Linear poly-bis-(trifluoro ethoxy)phosphazene	A	$[NP(OCH_2CF_3)_2]_n$	13	–	–	–

[a] Al_2O_3, Fe_2O_3, alkali and alkaline-earth oxides.

[b] Prevailing radius (r) according to Hg porosimetry in the range $r \geqslant 60$ nm.

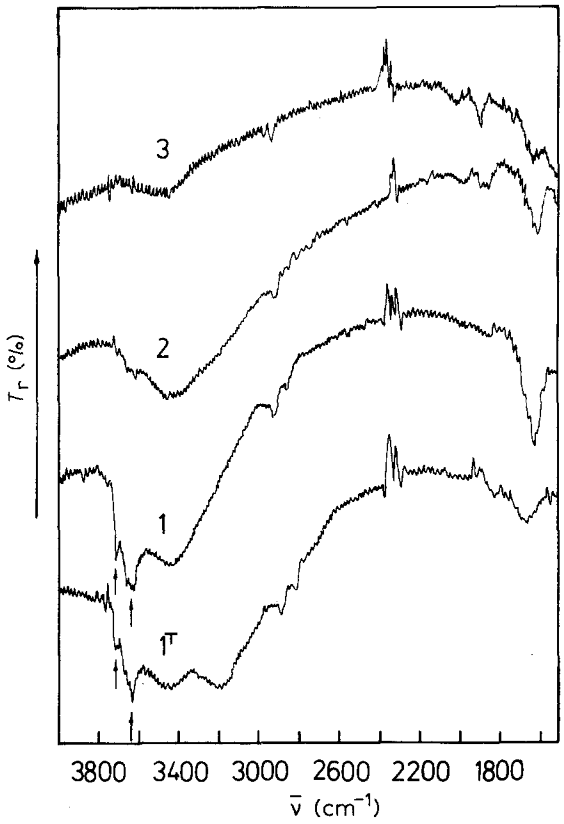

Figure 1 I.r. spectra (transmittance T_r versus wave number $\bar{\nu}$) of bare kieselguhr supports (1) No. 1, (2) No. 2, (3) No. 3 and (1^T) support No. 1 with a hexachlorocyclotriphosphazene deposit.

acetone for A. They were evaporated from the impregnated supports at room temperature and atmospheric pressure. One concentration value for the T solution and three different values (designated I, II, III) for the A solution were dealt with (Table II). The final step consisted in heating the phosphazene-carrying support as follows:

(i) T-loaded samples were transferred into glass tubes which were sealed under argon and left in an oven for 6 h at 180 ± 2 °C.

(ii) A-loaded samples were heated in air for 6 h at 140 ± 2 °C.

Surface area measurements followed the standard BET procedure with nitrogen at – 196 °C (Table II). The adsorption isotherms of water vapours at 22 °C were recorded by means of a McBain vacuum balance, the sensitivity of its spring being 6×10^{-3} g mm^{-1}. They are shown in Figs 2–6 below; the notation uses an arabic numeral (1, 2, 3) to specify the support and a supercript to point out the deposit, where T, I, II and III stand for T and solution concentrations I, II, III of A, respectively.

3. Results and discussion

3.1. General

Fig. 2 gives the adsorption isotherms of the bare supports (1, 2, 3) and the phosphazenes as individual

TABLE II Surface areas of bare and phosphazene loaded kieselguhr supports

Type of impregnation	Superscript in notation	Surface area ($m^2 g^{-1}$)		
		No. 1	No. 2	No. 3
None (bare kieselguhr supports)	None	24	40	0.8
Poly-bis-(trifluoroethoxy)phosphazene from acetone solution of concentration:				
3.7×10^{-2} wt %	I	33	36	0.8
3.7×10^{-1} wt %	II	38	31	0.9
3.7 wt %	III	5	20	0.4
Hexachlorocyclotriphosphazene (1.3 wt % diethyl ether solution)	T	5	21	0.4

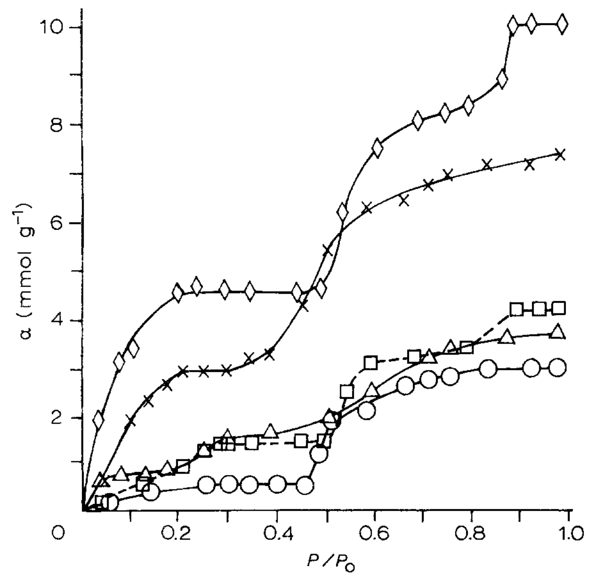

Figure 2 Adsorption isotherms (adsorbed amount per g, α, versus relative pressure p/p_0) for water vapour at 22 °C on (□) hexachlorocyclotriphosphazene, (◇) poly-bis-(trifluoroethoxy)phosphazene and bare kieselguhr supports (×) No. 1, (△) No. 2 and (○) No. 3.

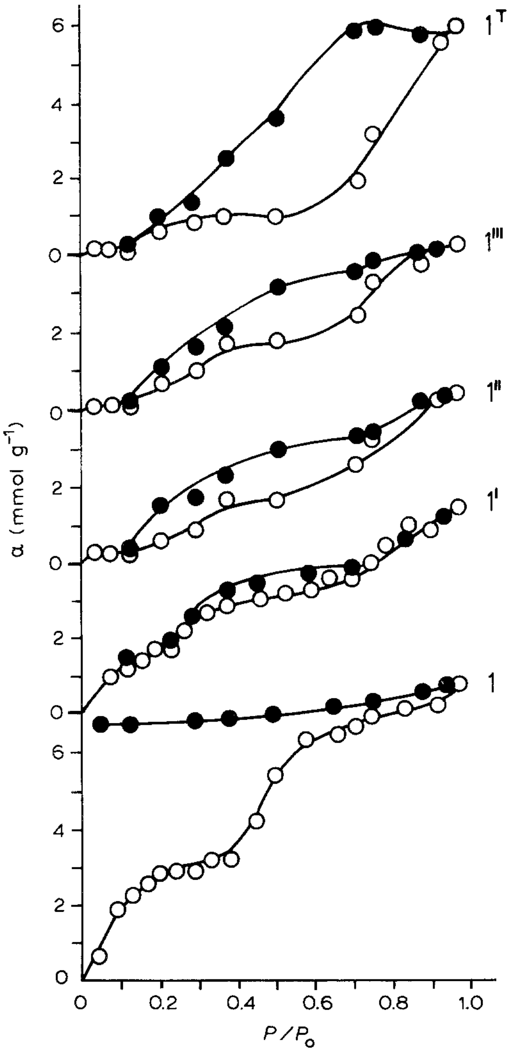

Figure 3 Adsorption isotherms for water vapours at 22 °C on bare and phosphazene-loaded kieselguhr supports No. 1: (1) bare, (1^T) hexachlorocyclotriphosphazene deposit, and poly-bis-(trifluoroethoxy)phosphazene deposited from acetone solutions of concentration (1^I) 3.7×10^{-2}, (1^{II}) 3.7×10^{-1}, (1^{III}) 3.7 wt %; (○) adsorption, (●) desorption.

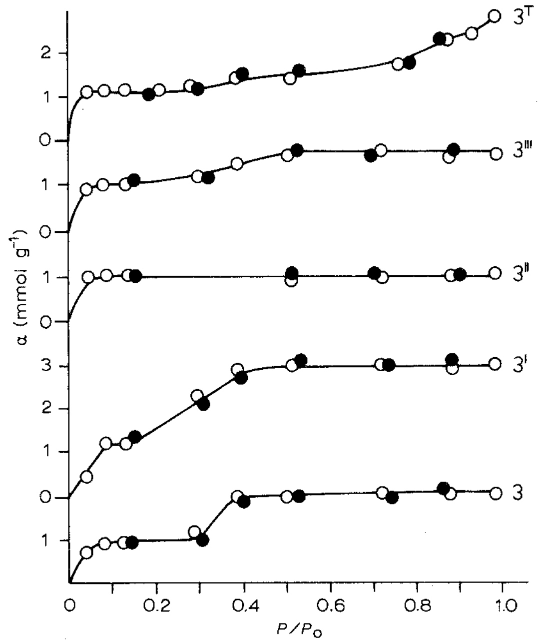

Figure 4 Adsorption isotherms for water vapour at 22 °C on bare and phosphazene-loaded kieselguhr supports No. 3: (3) bare, (3^T) hexachlorocyclotriphosphazene deposit, and poly-bis-(trifluoroethoxy)phosphazene deposited from acetone solutions of concentration (3^I) 3.7×10^{-2}, (3^{II}) 3.7×10^{-1}, (3^{III}) 3.7 wt %; (○) adsorption, (●) desorption.

substances (T, A). The sequence of adsorption capacities per unit weight of the support ($3 < 2 < 1$, Fig. 2) differs from that of their surface areas ($3 < 1 < 2$, Table II). Probably, this could be accounted for by the extra adsorption sites mentioned in section 2 (Al^{3+}, Na^+ etc.) which are characteristic of No. 1 but absent, apparently, from the surface of Nos 2 and 3. With this in mind, let us note that the adsorption on No. 1 has the feature of being irreversible (Fig. 3) which is not the case with No. 3 (Fig. 4) and No. 2 (not shown).

As to the phosphazenes, A proves comparable to No. 1 in both adsorption capacity and surface area, while T is not easy to compare because its surface area is orders of magnitude less than that of other samples.

3.2. Supported hexachlorocyclotriphosphazene (T)

When put on No. 1, T has the effect of reducing the surface area considerably (Table II) and making the adsorption reversible although a wide loop of adsorption–desorption hysteresis still remains (1 and 1^T, Fig. 3). With Nos 2 and 3 reduction of the surface area is less pronounced (Table II) whilst adsorption proves reversible and with no hysteresis loops, just as it is on the bare supports themselves (Fig. 4; No. 2 not shown). This would suggest T molecules blocking the entrance to a portion of the bottle-necked pores present in No. 1, or eventually some supposed constrictions for Nos 2 and 3. If irreversibility with No. 1 comes from the strongest adsorption sites they should be specific to No. 1 and absent from Nos 2 and 3; the extra adsorption sites of No. 1 could be considered its strongest ones, and hence the first to be covered by T molecules upon impregnation. Since adsorption on T alone is reversible, this will result in a reversible adsorption on T-loaded No. 1 supports, the hysteresis loops persisting as long as they are due to the intrinsic texture of this type of support, e.g. its bottle-necked pores.

Approximately, the amount of T introduced into the pores is 2.7×10^{-5} mol per cm^3 of pore volume. Thus on average a T molecule can have in its disposition a square area of length 1.42, 1.37 or 0.22 nm at the surface within the pores of support Nos 1, 2 or 3, respectively. As is known, the T molecule is planar and can be inscribed within a square of edge length 0.66 nm [13]. Therefore, lining of the pore walls with flat-lying T molecules is possible for Nos 1 and 2 whereas an island structure of the deposit has to be expected for No. 3. In any case, the deposit is likely to be in a state of high dispersion which favours reaching the full capacity of T in water adsorption.

In Figs 5 and 6 the adsorbed amount is referred to unit surface area. This allows us to infer that T-loaded kieselguhr supports are adsorbing larger amounts of water vapour than the supports alone in the whole range of relative pressure (p/p_0), sample 1^T for $0 \leqslant p/p_0 \leqslant 0.2$ providing the only exception. The latter fact is likely to mean that the extra adsorption sites of a bare support No. 1 are stronger than the T molecules covering them upon deposition. It is noteworthy that the adsorption isotherms on T-loaded kieselguhr supports (curves 1^T and 3^T; 2^T not shown) rise steeply at $p/p_0 \geqslant 0.7$, which is observed neither on bare supports (curves 1 and 3; 2 not shown) nor on T alone (cf. Fig. 2).

Comparison of the i. r. spectra 1 and 1^T in Fig. 1 and Fig. 7 suggests that chemical bonding of T molecules to kieselguhr surfaces is likely to occur too. Thus an Si–O–P fragment could be responsible for the absorption at 1400 cm^{-1} in Fig. 7.

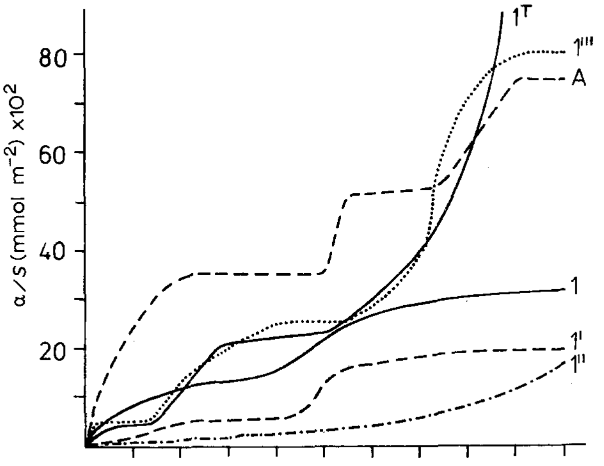

Figure 5 Adsorption isotherms per unit surface area for water vapour at 22 °C on (A) poly-bis-(trifluoroethoxy)phosphazene and on kieselguhr supports No. 1: (1) bare, (1^T) hexachlorocyclotriphosphazene deposit, and poly-bis-(trifluoroethoxy)phosphazene deposited from acetone solutions of concentration (1^I) 3.7×10^{-2}, (1^{II}) 3.7×10^{-1}, (1^{III}) 3.7 wt %.

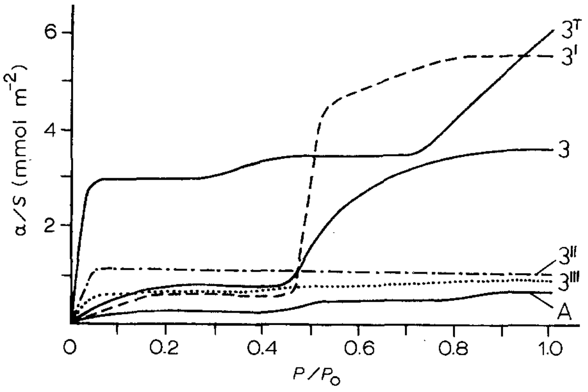

Figure 6 Adsorption isotherms per unit surface area for water vapour at 22 °C on (A) poly-bis-(trifluoroethoxy)phosphazene and on kieselguhr supports No. 3: (3) bare, (3^T) hexachlorocyclotriphosphazene deposit, and poly-bis-(trifluoroethoxy)phosphazene deposited from acetone solutions of concentration (3^I) 3.7×10^{-2}, (3^{II}) 3.7×10^{-1}, (3^{III}) 3.7 wt %.

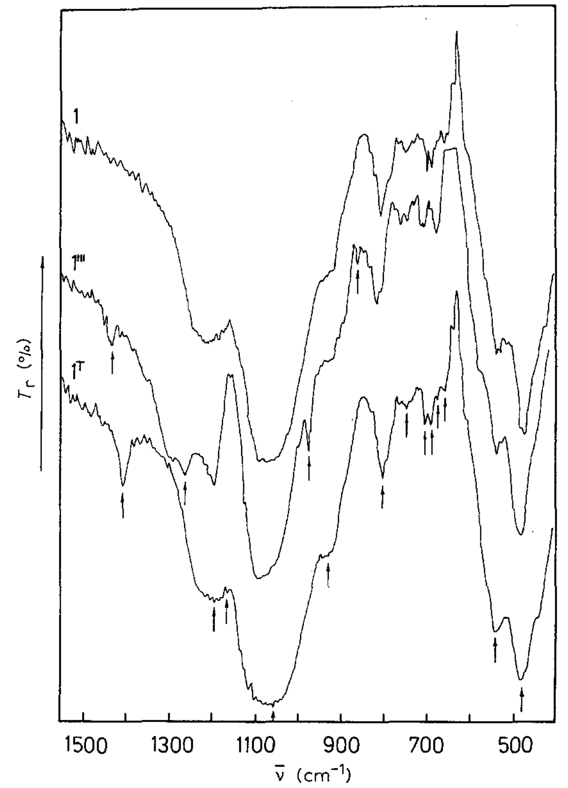

Figure 7 I.r. spectra (transmittance T_r versus wave number $\tilde{\nu}$) of kieselguhr supports No. 1: bare, (1^T) hexachlorocyclotriphosphazene deposit, (1^{III}) poly-bis-(trifluoroethoxy)phosphazene deposited from 3.7 wt % acetone solution.

3.3. Supported poly-bis-(trifluoroethoxy) phosphazene (A)

Fig. 7 compares also the i.r. spectrum 1^{III} of an A-loaded sample with that of the bare support (curve 1).

A striking feature of A deposition is the increase in surface area with support No. 1 at lower concentrations of the polymer solution, although with Nos 2 and 3 the surface areas simply diminish showing no maximum (Table II). Another one is the superadditivity of the adsorption capacity per unit surface area of sample 3^I with respect to its constituent parts No. 3

and A for $p/p_0 > 0.45$ (Fig. 6). This seems to imply dependence of the adsorption behaviour of A molecules on their conformation which is not necessarily the same for the crystalline solid state (up to 242 °C [13]) and within the pores of kieselguhr matrices under various conditions. In turn, a few assumptions about these conformations may be tested in order to explain the data.

With support No. 1 the effect of A deposition on adsorption–desorption irreversibility and hysteresis is qualitatively the same as that of T deposits (Fig. 3), probably for similar reasons. However, adsorption of A molecules on pore walls brings about a drastic change in their conformation in comparison with the solid-state A sample. As is known, such an adsorbed molecule, in the ideal chain approximation, consists of a dense globule centred at the adsorption site and rimmed with a set of loops filling a hemisphere of root-mean-square radius h given by

$$h = \frac{a}{\sqrt{(\lambda - 1)}} = \frac{4.12a}{1 - 3.52\exp(-\varphi)} \qquad (1)$$

Here $(\lambda - 1)^{-1/2}$ is the number of chain segments in the average loop, a denotes segment length and $\varphi > 0$ stands for the depth of the potential well causing adsorption. Note that φ is expressed in $k_B T_{ads}$ units (k_B = Boltzmann constant, T_{ads} = absolute temperature); obviously, when $\lambda \to 1$, i.e. at $\varphi \simeq 1$, adsorption becomes impossible ($h \to \infty$) [14]. In the crystalline state, A molecules adopt a nearly *cis–trans* planar conformation [13], the repeating unit $[NP(OCH_2CF_3)_2]_2$ being of length $b = 0.483$ nm. For the sake of estimation we put $a = 5b$.

Protruding hemispheres on flat pore walls mean a corrugated surface and hence an increase in surface area. In addition, they are likely to show hydrophobicity because repulsive interaction of bulky $-OCH_2CF_3$ substituents will tend to place the latter on the outer side of loop contours.

Roughly speaking, the amount of A introduced into the pores from solutions of concentrations I, II, and III is of the order of 10^{14}, 10^{15} and 10^{16} molecules per cm^3 of pore volume, respectively. With support No. 1 this mean that on the average an A molecule can have in its disposition at the surface within the pores a square domain of length 562, 178 or 56 nm according to concentration I, II or III, respectively. From Equation 1 one obtains $h < 50$ nm for adsorption sites of strength $\varphi > 1.5$. In other words, even for concentration III all A molecules could be accommodated on pore walls provided the walls possess the required number of adsorption sites. If this latter condition is not fulfilled, a portion of the molecules will have to dwell in the bulk of pores. The conformation they will take there depends on the pore width [15, 16]. Because the supports studied have extremely wide pores the random coil model seems appropriate to represent the chain of A molecules in the bulk of the pores.

Accordingly, the root-mean-square end-to-end distance (r_0) for such a coil is $r_0 \simeq N^{3/5}a$, where N denotes the number of chain segments and the exponent (3/5 instead of 1/2 for the ideal chain) takes into account excluded volume repulsion [14]. With a contour length L of approximately 1.69×10^3 nm and $N = L/a$ one obtains $r_0 \simeq 123$ nm, a value much smaller than the pore width; in constrictions the coil will be correspondingly compressed. Since the coil volume per chain segment in a^3 units amounts to 190, the coil proves a rather spacious structure allowing the chain to reach its maximum capacity for water uptake by full involvement of nitrogen and phosphorus adsorption sites from the backbone. At the same time this is a conformation rather different from that in the crystalline solid state. The inference is twofold: first, the overall adsorption behaviour of A within the pores will depend on the partition between random coil and rimmed globule conformations, the same applying to effects on the support itself; second, under the circumstances comparison with adsorption per unit surface area of solid-state A samples may or may not be meaningful.

Fig. 5 gives adsorption isotherms for bare and A-loaded support No. 1 per unit surface area. With increasing amount of A introduced into the pores ($1 < 1^{I} < 1^{II}$) the curves go down to the p/p_0 axis although the surface areas augment ($1 < 1^{I} < 1^{II}$, Table II). This could be due to A molecules adopting in growing numbers the rimmed globule conformation, let alone their blocking the strongest adsorption sites of the support. Curve 1^{III} would imply the appearance of A molecules in the hydrophilic conformation of random coils, with a portion of them dwelling in narrower pores and/or constrictions which are thus excluded from adsorption (surface area reduction).

It can be seen from Fig. 6 that with the smallest A deposit support No. 3 becomes at $p/p_0 \geqslant 0.5$ (3^{I}) much more hydrophilic than both the bare support (3) and the solid-state A sample (A), but further increase in the deposited amount directs the course of adsorption (3^{II}, 3^{III}) to that on the A sample. Initially extended A coils packing more and more densely with growth of the deposit seem to account for this trend.

Support No. 2 by itself is approximately as good at water adsorption as the A deposit on it (the data have not been plotted).

4. Conclusions

(a) Very small amounts of hexachlorocyclotriphosphazene ($\sim 10^{-3}$ wt %) as well as of linear poly-bis-(trifluoroethoxy) phosphazene (from 10^{-2} to 1 wt %) deposited on various diatomaceous earth supports improve the adsorption capacity per unit surface area of the latter.

(b) Deposition of the phosphazenes, converting them to high dispersion, favours reaching their own full capacity for water adsorption.

(c) The adsorption behaviour of poly-bis-(trifluoroethoxy)phosphazene deposits and their effect on the support can be treated in terms of two conformations of the polymer chain within the pores: a surface-attached rimmed globule and a bulk-dwelling random coil.

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