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ADSORBENTS FOR GAS-SOLID CHROMATOGRAPHY PREPARED BY EPITAXIAL MODIFICATION OF CLAY MINERALS WITH QUATERNARY AMMONIUM IONS

MARCO TARAMASSO

SNAM Progetti-LSR, San Donato Milanese (Italy)

SUMMARY

The epitaxial growth of a phase over a heterogeneous crystalline matrix is proposed in order to obtain homogeneous adsorbents able to show both steric effects and specific interactions.

The properties required by both phases in order to produce stable derivatives are examined. Examples are given of the epitaxial modification of mica-type layered silicates with N-alkylpyridinium and *n*-alkylammonium ions. Some unpublished and published results are reviewed for derivatives containing dimethyldioctadecylammonium and trimethylhexadecylammonium ions.

The work of KISELEV AND YASHIN¹ demonstrates the great potentiality and, until now, far from complete exploitation that the gas-solid chromatography offers in difficult separations of geometric and steric isomers. Principally, the need is for new homogeneous and selective adsorbents.

Chemical modification of heterogeneous adsorbents both by coating surfaces with liquids and by grafting radicals to active centres, has been studied extensively. However such modification results in disordered surfaces and the peculiarity proper to a surface of rigid geometry is lost; in other words, the difference in adsorption enthalpy for isomeric forms disappears.

I should like to discuss the promising possibility offered by epitaxial growth of a phase over a heterogeneous crystal, in order to obtain homogeneous adsorbents able to show steric effects as well as specific interactions.

Epitaxial modification, *i.e.*, an ordered arrangement along the crystal axes, requires a suitable matrix with appropriate binding points (active groups or lattice vacancies) in order to establish either stable chemical or electrostatic bonds with the growing phase. On the other hand the radicals or ions, which are to be linked to the crystal faces, must be big enough so as to ensure complete coverage of the surface and to allow such a dense packing that free molecular rotation of the grafted groups is prevented.

A simple example of epitaxial modification is given by the organic derivatives of the clay minerals. Among the latter, the family of mica-type layer silicates are

of interest. They possess a sheetlike structure resulting from a lattice constituted of an octahedral layer containing either alumina or magnesia, sandwiched between two tetrahedral layers of silica². A charge deficit within the lattice can be found as a result of isomorphous substitution by ions of lower valency. Electrical neutrality is then ensured by the presence of counter ions held on the basal surfaces; these ions are subject to displacement by means of ionic exchange reactions. The exchangeable cation concentration depends upon the nature of the mineral: consequently the "equivalent area", that is the surface available for each univalent cation, varies from infinite (*e.g.* for pyrophyllite) to 24 \AA^2 (*e.g.* muscovite).

Let us look at an example: if a clay of large equivalent area (of about 100 \AA^2 , *e.g.* a montmorillonite) is exchanged with pyridinium ions, only about $1/4$ of the available surface is covered. While the adsorbent obtained is heterogeneous, it nevertheless shows an interesting selectivity which resembles a sieve action: for instance 1,4-dimethylcyclohexane in the *trans* form is retained more than the *cis* isomer, the relative volatility being as high as $\alpha = 8$ at 150° ; the first peak is symmetrical and the separation is of practical interest. The elution order of the xylenes is: *meta* then *para*, the reverse of that obtained with alkylammonium derivatives: both peaks are strongly asymmetrical and the retentivity depends on the sample amount.

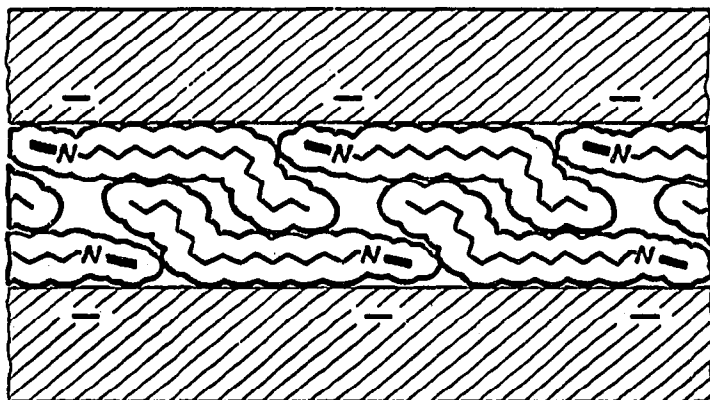


Fig. 1. Model for the arrangement of N-*n*-alkylpyridinium ions between silicate layers³.

Now, if N-*n*-alkylpyridinium ions are used in place of the simple pyridinium ion, when the alkyl chain is 10 carbon atoms long, the above mentioned clay, with about 100 \AA^2 of equivalent area, is completely covered since the alkyl chain lies flat on the silicate surface. Increasing the length of the chain results in the chain overlapping the aromatic ring³, as shown in Fig. 1. The adsorbent thus obtained behaves like an homogeneous one: the selectivity towards the *cis-trans* forms of dimethylcyclohexane is lost; the xylenes elute in the order *para*, *meta*, with symmetric peaks ($A_s = 1.2-1.5$) and a relative volatility at 100° , $\alpha = 1.2-1.3$. A new selectivity order also appears: ethylbenzene is retained more than *p*-xylene, contrary to what occurs with the alkylammonium derivatives. The efficiency of N-alkylpyridinium columns is low (HETP = 0.4-0.6 cm).

The structure of the *n*-alkylammonium derivatives has been studied in greater detail than that of any other organic cation⁴. The preferred arrangement of the alkyl chains, on a clay having a medium equivalent area, is the *trans-trans* configuration.

The bonding strength is high: in addition to coulombic forces, N-H...O hydrogen bridges are formed with the oxygen surface of the silicate sheet. The organic cations slope at an angle of 56° to the basal plane.

Unfortunately, from the gas chromatographic point of view derivatives of this kind behave homogeneously ($As = 1.2$) with highly charged silicates only (beidellites and vermiculites, equivalent area: 50–35 Å²); besides the specificity is low (*m*- to *p*-xylene: relative volatility at 130°, $\alpha = 1.2$).

Bulky cations as trimethylhexadecylammonium or dimethyldioctadecylammonium are convenient owing to both their basic character and their good surface covering power⁵. As the dimethyldioctadecylammonium ion is able to cover at least 200 Å² of surface, the complexes obtained with all the clay minerals belonging to the groups from hectorite to biotite (the equivalent area varying from 100 to 24 Å²) behave as homogeneous adsorbents in gas chromatography: thus accurately prepared derivatives give symmetric peaks and do not require the addition of modifying liquids. Table I shows the most significant values obtained with representative members of each group. When an excess of dimethyldioctadecylammonium halide

TABLE I

PROPERTIES OF SOME REPRESENTATIVE DIMETHYL-DIOCTADECYLAMMONIUM DERIVATIVES OF MICA-TYPE LAYER SILICATES

Equivalent Minerals area (Å ²)		(C ₁₈ H ₃₇) ₂ (CH ₃) ₂ N ⁺ derivatives		
		C.E.C. (mequiv./g clay)	X-ray basal spacing (Å)	meta-paraxylene relative volatility, 130°
100	Hectorite, Hector	0.88	24.0	1.2
80–45	Montmorillonite, Sarighyuhski	1.18	25.8	1.2 ₆
	Montmorillonite, Pizhev	1.35	27.1	1.4
	Saponite, Groschlattengrun	1.19	29.4	1.4
	Nontronite, Andreasberg	0.83	29.6	1.5
	Beidellite II, Unterrupsroth	0.97	36.0	1.6
45–37	Vermiculite, Young River	1.08	33.3	1.6 ₆
	Vermiculite, South Africa	0.62	n.i.e. ^b	1.6
38–28	Illite, Fuzèrradvány	0.39	n.i.e.	1.3
28–23	Muscovite	n.d. ^a	n.i.e.	1.1
	Biotite from Don basin	0.14	n.i.e.	1.0 ₆

^a n.d. = not determined.

^b n.i.e. = no interlayer exchange.

solution is used for the exchange reaction, the X-ray basal spacing, for derivatives in the dry state, is 36–37 Å in every case. By removing the excess of the intercalated salt the basal spacing decreases to 24–26 Å with montmorillonitic minerals and to 29–37 Å with beidellitic and vermiculite minerals. This suggests a different arrangement of the organic cations depending on the different values of the equivalent area of the clay mineral used. The gas chromatographic effectiveness (for instance the

m- to *p*-xylene relative volatility) increases as the basal spacing increases, therefore it appears to be directly related to the packing density of the organic cations (see Table I). Thus the best results are obtained with beidellite and vermiculite type derivatives. With clay minerals having low equivalent areas ($\leq 37 \text{ \AA}^2$) the exchange only occurs on the external basal surfaces, without any interlamellar penetration (e.g. as in the case of South African vermiculite and Fuzèrràdvány illite). As the equivalent area decreases (24 \AA^2 or less: biotite, mica) and when the counter ion is K^+ , the exchange becomes incomplete and unsatisfactory gas chromatographic results are obtained, unless more sophisticated procedures in preparing the derivatives are adopted⁶.

The specificity of "beidellite type" dimethyldioctadecylammonium derivatives towards molecules containing π -bonds is illustrated by the separation of cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene and benzene (Fig. 2).

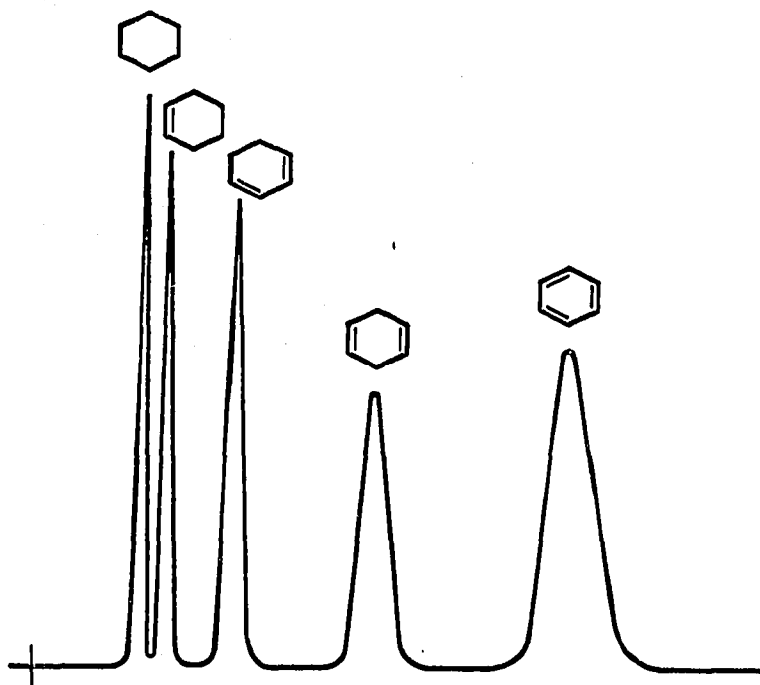


Fig. 2. Separation of cyclohexane; cyclohexene; 1,3-cyclohexadiene; 1,4-cyclohexadiene and benzene on dimethyldioctadecylammonium vermiculite (South Africa). Column length 1.9 m. Packing 15% wt. of organic derivative on Chromosorb P, 60-80 mesh. Temperature 95° ; carrier gas H_2 at 60 ml/min.

The relative volatility value of 1.7-1.8 and the peak symmetry obtainable at 130° for the pair, *m*- and *p*-xylene, with the beidellite type derivatives are noticeably higher than that obtained with the known Bentone 34 (1.26 at 70°). Fast separations are obtained with derivatives which do not possess an interlayer phase, as shown in Fig. 3 (see also ref. 5). Further information concerning the separation of complex mixtures is given in ref. 7. The steric effects due to the epitaxial arrangement of the organic cations are evident in the separation of the trimethylbenzenes; these are eluted in the order 1,3,5-, 1,2,4- and 1,2,3- on pure alkylammonium halide while they are separated on beidellite type derivatives in the reverse order⁵.

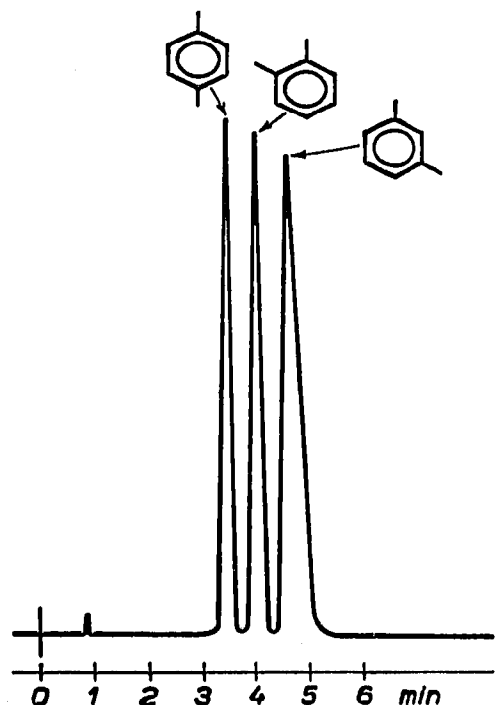


Fig. 3. Fast separation of xylene isomers on dimethyldioctadecylammonium illite (Fuzèrradvány). Temperature 140° . Other conditions as in Fig. 2.

In the range from 30 to 50° every dimethyldioctadecylammonium derivative shows a reversible characteristic transition. This was first noticed by gas chromatography, since the separation of *cis-trans* olefines does not occur below the transition temperature. The transition is never sharp, and annealing is necessary before reproducible behaviour is obtained with a differential scanning calorimeter. The results are tentatively explained in terms of hindered rotations around carbon-carbon bonds following an approach originally suggested by TEMPERLEY⁸ for hydrocarbon-like polymers.

The entropy contribution for each such kink is compared to the total entropy change. It is found that 8-17 bonds are subjected to kinks whereas simple dimethyldioctadecylammonium chloride, in absence of clays, has 35 bonds subjected to torsion. One would conclude that it is not a matter of fusion in the usual meaning of the word: the disorder is limited to a section of the chain only.

From the gas chromatographic point of view, the transition does not influence the elution order, but only the column efficiency, following the sudden increase of peak asymmetry values from 1 to 2 and even higher values. At the same time the isotherm shape varies from sigmoid (Brunauer type) to the anti-Langmuir form, below the transition temperature, as is shown by the benzene isotherm at 42° on dimethyldioctadecylammonium vermiculite (South Africa) (see Fig. 4). Such isotherms represent a limiting case due to the absence of an interlayer organic phase. Fully exchanged clay minerals tend to approach linearity owing to the greater capacity. However in every case the linearity is limited to the higher temperatures and to the inferior portion of isotherm corresponding to the lower concentrations. In such a range, some evidence⁷ suggests that both aromatic and saturated hydrocarbons are

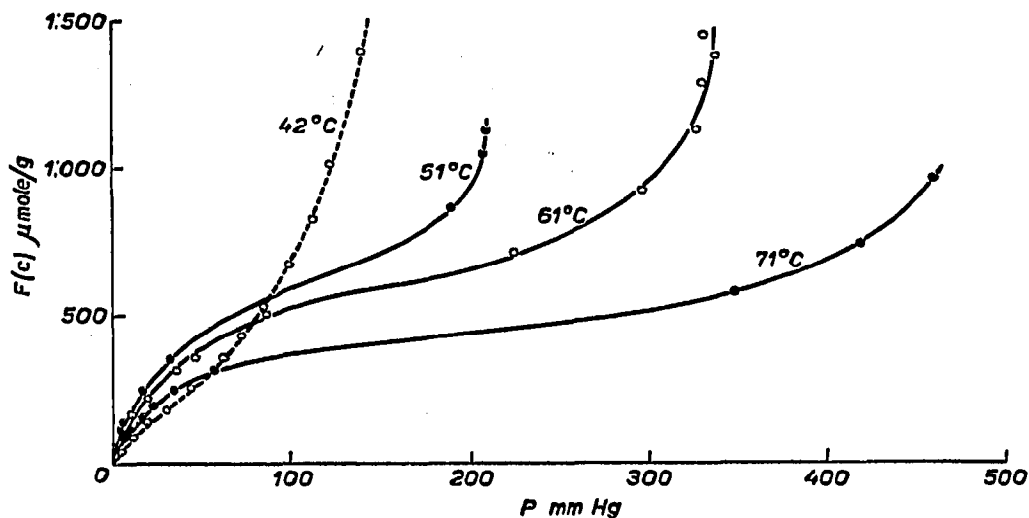


Fig. 4. Isotherms of benzene on dimethyldioctadecylammonium vermiculite (South Africa). Concentration, $F(c)$, of the adsorbate in the adsorbent as a function of the partial pressure P .

adsorbed on a homogeneous surface of paraffinic chains and that they maintain a great degree of translational freedom at the surface.

With regard to the surface arrangement of the dimethyldioctadecylammonium ions, a few plausible models can be suggested⁷. Fig. 5 shows two extreme situations such as arise with high and low equivalent area clays. The picture refers to the inter-lamellar space, but even on the outer surface, were the available space doubled, a

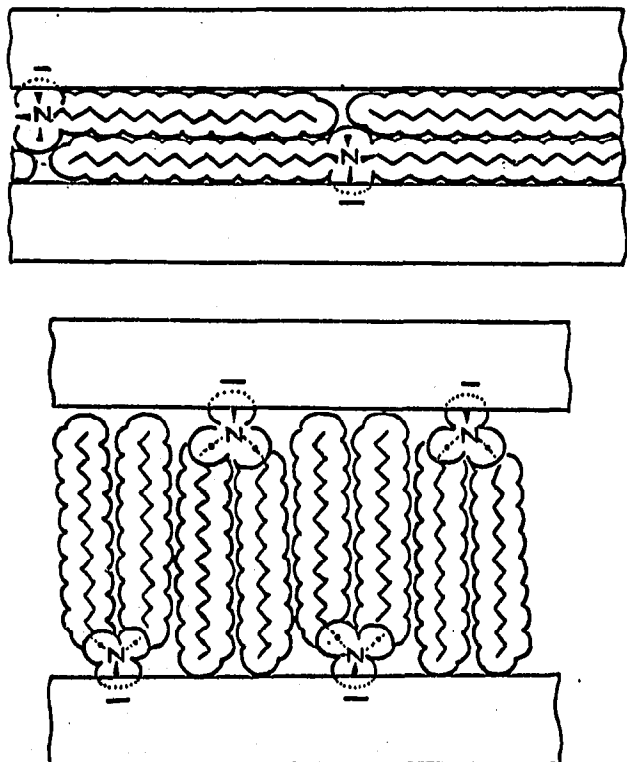


Fig. 5. Idealized models for the arrangement of dimethyldioctadecylammonium ions between the lamellae of (upper) a large and (lower) a small equivalent area clay mineral.

number of skew-chains are to be postulated with the most crowded clay surfaces.

Recent X-ray data indicate that the dimethyldioctadecylammonium ions penetrate between the lamellae with the long alkyl chains contacting the surface, when markedly underequivalent amounts of solution are used. As larger and larger amounts of organic molecules are grafted to the silicate, basal spacing increases progressively, thus suggesting that the alkyl chains are lifted from the surface. In addition, basal spacing measurements on a series of $R_2(CH_3)_2N^+$, in which the n -alkyl, R , varies from C_8 to C_{18} , suggest that the organic cation slopes at an angle of 60 – 70° to the surface (see Table II).

With a view to explaining the elution order of various hydrocarbons by means of the corresponding sequence of experimental and calculated heats of adsorption, an intermediate situation has been assumed for the arrangement of the alkylammonium ions. Adsorption energies on several positions have been evaluated and aver-

TABLE II

X-RAY DATA ON $R_2(CH_3)_2N^+$ BEIDELLITE (UNTERRUPSTROTH) DERIVATIVES (EQUIVALENT AREA OF BEIDELLITE U.: 54 \AA^2)

$R = \text{No. C}$	Basal spacing (\AA)	Spacing of organic interlayer (\AA)	Height of the alkyl chain sloping at 70° to the surface (\AA)
8	22.7	13.3	14.5
10	21.4	12.0	16.5
12	29.0	19.6	18.5
14	32.0	22.6	20.5
16	29.0	19.6	22.5
18	36.0	26.6	24.5

aged⁵. Experimental isosteric heats of adsorption for n -paraffins fall within the range 0.2 – 0.5 kcal for all minerals studied. Theoretical values are seen to agree satisfactorily with the experimental ones. That the interaction with saturated hydrocarbons has been calculated correctly is again verified in the case of alkylbenzenes on hectorite; conversely results for aromatic compounds such as benzene, toluene and xylenes are very uncertain. In these cases the electrostatic interaction energies have been calculated without taking into account the polarisability anisotropy. As the information concerning the electric field intensity at various lattice positions is inadequate, the assumptions just made possibly have only a limited validity.

From what has been said it may be inferred that organic derivatives of clay minerals, having better selectivity, can be obtained by increasing the surface concentration of the organic cations and the distance of the positive charge from the clay surface, as preliminary results with other alkylammonium ions appear to indicate. Thus for example, treatment of natural K-biotite with sodium tetraphenylboron to give Na-biotite results in an increased final content of trimethylhexadecylammonium ions, with a corresponding increase in the m -/ p -xylene relative volatility to 2.2 at 130° .

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