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## RETENTION OF HYDROCARBONS ON GAS CHROMATOGRAPHIC SORBENTS CONTAINING AN ORGANO-CLAY\*

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### SUMMARY

The equations describing retention on a combined sorbent containing a solid adsorbent and a stationary liquid phase (SLP) have been obtained on the basis of a theory of retention developed earlier. Experimental methods have been proposed for estimating the relative roles of dissolution and adsorption for combined sorbents based on organo-clays. The distribution coefficients of  $C_6-C_{10}$  hydrocarbons between a carrier gas and an SLP layer, SLP surfaces, a solid support and organo-vermiculite, and SLP-solid support and SLP-organovermiculite interfaces have been determined.

The selectivity of adsorption in the separation of the pairs benzene-cyclohexane and *m*-xylene-*p*-xylene has been studied for sorbents containing pure and impregnated organovermiculites. It has been shown that the selectivity depends on the polarity of the SLP.

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### INTRODUCTION

The use of combined sorbents containing a solid adsorbent, a stationary liquid phase (SLP) and a solid support increases the possible applications of gas chromatography as selectivity can be controlled simply by varying the proportions of the constituents of the combined sorbent. However, it is difficult to choose the most suitable proportions as changes in sorbent characteristics are not additive. It is necessary to take into consideration modifications of the adsorbent by the SLP and changes in sorptive properties of SLP thin layers effected by the solid support<sup>1</sup>.

Combined sorbents of the above type, containing an organo-clay and an SLP, are widely used in gas chromatography for the separation of aromatic isomers<sup>2-4</sup>. However, until recently no research had been devoted to the retention mechanism and no quantitative estimation of the roles of adsorption and dissolution had been made. In addition to Bentone 34, studied as early as 1957<sup>5</sup>, more selective organo-clays have been proposed, particularly those based on vermiculite<sup>6,7</sup>. Gas chromatographic in-

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vestigations with various organo-clays have shown that the vermiculite derivatives based on vermiculite from a deposit in the Soviet Union (Kovdor) have improved the selectivity (compared with commonly used bentonites) towards aromatic hydrocarbons in general and also some of their isomers<sup>8</sup>.

In the light of the above earlier work, it was considered of interest to investigate the retention mechanism on a combined sorbent containing a highly selective organo-vermiculite.

#### RETENTION ON SORBENTS CONTAINING AN ORGANO-CLAY AND A STATIONARY LIQUID PHASE ON A SOLID SUPPORT

The general theory of retention on adsorption-active solids impregnated with SLPs has been discussed earlier<sup>9,10</sup>. The equation describing the net retention volume as a sum of retention volumes on sorbent constituents for a sorbent based on an organo-clay and an SLP is

$$V = k_{GS}s_{GS} + k_{GA}s_{GA} + k_{GL}s_{GL} + k_S s_{LS} + k_A s_{LA} + k_L v_L \quad (1)$$

where  $V$  is the net retention volume,  $k_{GS}$  and  $k_{GA}$  are the distribution coefficients of a substance between the carrier gas and the uncoated surfaces of the solid support and the organo-clay, respectively,  $k_S$  and  $k_A$  are the distribution coefficients between the carrier gas and the surfaces of the solid support and the organo-clay coated with SLP, respectively,  $k_{GL}$  is the distribution coefficient between the carrier gas and the gas-SLP interface,  $k_L$  is the distribution coefficient between the carrier gas and an SLP layer,  $s_{GS}$ ,  $s_{GA}$ ,  $s_{GL}$ ,  $s_{LS}$  and  $s_{LA}$  are the areas of the gas-solid support, gas-organoclay, gas-SLP, SLP-solid support and SLP-organoclay interfaces, respectively, and  $v_L$  is the SLP volume.

Consideration of the cases that can be realized in practice simplifies eqn. 1 (Table I).

For practical purposes, it is convenient to use, firstly, the retention volumes calculated per unit mass of the solid support in the column ( $V_N = V/m_s$ ), and secondly, the distribution coefficients calculated per unit mass of the sorbent constituents for characterizing sorptive processes:

$$K_{GS} = k_{GS}\sigma_s, K_{GA} = k_{GA}\sigma_A \text{ and } K_L = k_L/d \quad (2)$$

where  $\sigma_s$  and  $\sigma_A$  are the specific surface areas of the solid support and the organo-clay,

TABLE I  
VARIATION OF EQN. 1 FOR DIFFERENT SORBENTS

Sorbent	Variant of eqn. 1
Organo-clay on solid support	$V = k_{GS}s_{GS} + k_{GA}s_{GA}$
SLP on solid support*	$V = k_{GL}s_{GL} + k_S s_{LS} + k_L v_L$
Organo-clay and SLP on solid support*	$V = k_{GL}s_{GL} + k_S s_{LS} + k_A s_{LA} + k_L v_L$

\* SLP coats solid support and organo-clay completely

respectively, and  $d$  is the specific gravity of the SLP. Thus, for example, for sorbents with pure and impregnated organo-clays, the following equations are valid:

$$V_N = K_{GS} + K_{GA}P_A \quad (3)$$

$$V_N = z + K_A P_A + K_L P_L \quad (4)$$

where  $P_A = m_A/m_S$ ,  $P_L = m_L/m_S$ ,  $m_A$ ,  $m_L$  and  $m_S$  are the masses of the organo-clay, SLP and solid support, respectively, in the column, and  $z = K_{GL} \cdot (s_{GL}/m_S) + K_S \cdot (s_{LS}/m_S)$  is the contribution of adsorption on the gas-SLP and SLP-solid support interfaces.

In order to characterize the sorbent selectivity, use is made of the relative retention volumes. In the case of a "monophase" sorbent, this value is considered as the ratio of the distribution coefficients of two compounds. If, for example, in a sorbent that contains only an organo-clay, adsorption on a solid support is negligibly small ( $K_{GS} \ll K_{GA}P_A$ ), then the relative retention volume, in accordance with eqn. 3, is

$$V_{rel.} = K_{GA, rel.} = K'_{GA}/K''_{GA} \quad (5)$$

In order to study selectivity caused by different processes in a sorbent that contains an organo-clay and an SLP, it is advisable to determine the distribution coefficients and to calculate their ratio. Thus, for adsorption on an SLP-organoclay interface, we have:

$$K_{A, rel.} = K'_A/K''_A \quad (6)$$

Comparison of selective adsorption on the surface of a pure organo-clay and an organo-clay impregnated with SLP is of special interest.

The distribution coefficients can be determined under the condition that they are constant, *i.e.*, when  $P_A$  and  $P_L$  are varied over the range where they affect mainly one process. Thus, for example, in order to study dissolution, the amount of SLP must be sufficiently large for complete coating of the sorbent surface and the formation of a fairly thick layer to occur. If these conditions are satisfied, the dependences of the retention volumes on  $P_A$  and  $P_L$  are linear functions of the type  $V_N = A + B_L P_{(A,L)}$ . When  $P_L$  is a variable at constant  $P_A = \bar{P}_A$ , we obtain, in accordance with eqn. 4, the relationships between the linear dependence parameters and the distribution coefficients:

$$A = z + K_A \bar{P}_A \text{ and } B = K_L \quad (7)$$

Experimental confirmation of the linearity of these functions would support the validity of the chosen model of the sorbent structure and determination of their parameters would serve as a basis for determining the distribution coefficients.

It should be noted that the distribution coefficients may depend on the concentration of a substance in the carrier gas if the sorption isotherms are non-linear. The possibility of determining partial retention volumes and using them in plotting

the sorption isotherms on the SLP-organoclay interface has been shown earlier<sup>11</sup>. If the concentration in a carrier gas is small, the sorption isotherm for aromatic hydrocarbons on impregnated and non-impregnated organoclay is described satisfactorily by an equation of the Langmuir type. This was confirmed by chromatographic and static methods<sup>11</sup>. In this instance, the dependence of the net retention volume,  $V_{GA}$ , on the gas-adsorbent interface on concentration,  $c$ , in the carrier gas is expressed by the equation

$$V_{GA} = K_{GA}m_A = a_m b / (1 + bc)^2 \quad (8)$$

where  $a_m$  and  $b$  are the constants of the Langmuir equation. The equation for the partial retention volume on the SLP-adsorbent interface is similar to eqn. 8. It is evident that in order for invariance of the retention volumes to be attained, experiments must be conducted at a small dose rate ( $c \approx 0$ ), *i.e.*, when  $V_{GA} \approx a_m b$ .

## EXPERIMENTAL

### Apparatus

An LKhM-7A gas chromatograph (Mosneftekip, Moscow, U.S.S.R.) with a katharometer and a 3 m  $\times$  0.4 cm I.D. column was used. The detector and evaporator temperatures were 125° and 260°, respectively. Helium was used as the carrier gas at a flow-rate of 30–43 cm<sup>3</sup>/min.

### Compounds

Cyclohexane, *n*-nonane, *n*-decane, benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylene and cumene were used with a dose rate of 0.1  $\mu$ l.

### Organo-clays

Dimethylbenzylalkylammonium (DMBA) and dimethyldioctadecylammonium (DMODA) derivatives of vermiculite from Kovdor, U.S.S.R., and DMODA vermiculite from South Africa were used. DMBA and DMODA vermiculites were obtained by cation exchange between vermiculite and an aqueous solution of DMBA or DMODA chloride according to the procedure described by Taramasso and Veniale<sup>6,7</sup>.

### Stationary liquid phases

Dinonyl phthalate (DNP), dibutyl tetrachlorophthalate (DBT), mineral oil and diisooctyl sebacate (DIS) were used.

### Solid support

The solid support was Chromosorb P (60–80 mesh), silanized.

The sorbent was prepared by stirring a weighed amount of the organoclay with a benzene solution of the SLP for about 2 h. The suspension obtained was mixed with Chromosorb P and heated until the benzene had evaporated.

The net retention volume calculated per unit mass of solid support was obtained by the equation

$$V_N = j\theta qt/m_s \quad (9)$$

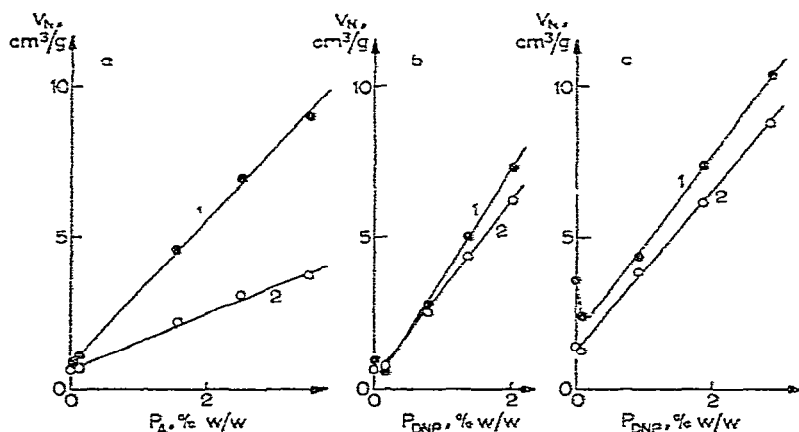


Fig. 1. Net retention volumes calculated per solid support mass as a function of DMBA vermiculite and DNP content at 84°. (a)  $P_{DNP} = 0$ ; (b)  $P_A = 0$ ; (c)  $\bar{P}_A = 0.89$  wt.%. 1, Ethylbenzene; 2, *n*-nonane.

where  $j$  is the compressibility correction factor,  $\Theta$  is the product of the correction for the water vapour pressure in a soap flow meter and corrections for reducing to normal conditions;  $q$  is the flow-rate of the carrier gas,  $t$  is the corrected retention time and  $m_s$  is the mass of the solid support.

## RESULTS AND DISCUSSION

The retention of hydrocarbons was studied on sorbents containing DMBA vermiculite and DNP or DBT at 84°.

The retention volumes calculated by eqn. 9 were used for plotting retention volume *versus* the content of organo-clay or SLP, as shown in Fig. 1. The dependence over the range of small values of  $P_{DNP}$  is shown by the dashed line in Fig. 1c. For cyclohexane and *n*-decane, the graphs were similar to that for *n*-nonane, and those for aromatic hydrocarbons were similar to that for ethylbenzene.

TABLE II  
PARAMETERS  $A_i$  AND  $B_i$  AND CONFIDENCE LIMITS\* FOR SORBENTS CONTAINING DMBA VERMICULITE (KOVADOR) AND DNP

Dependence	Compounds	$A_i \pm \Delta A_i$ ( $\text{cm}^3/\text{g}$ )	$B_i \pm \Delta B_i$ ( $\text{cm}^3/\text{g}$ )
$V_N = A + BP_A, P_{DNP} = 0$	<i>n</i> -Nonane	$0.60 \pm 0.06$	$90 \pm 5$
	Ethylbenzene	$1.00 \pm 0.07$	$230 \pm 20$
$V_N = A + BP_{DNP}, P_A = 0$	<i>n</i> -Nonane	$0.3 \pm 0.1$	$290 \pm 7$
	Ethylbenzene	$0.2 \pm 0.1$	$365 \pm 10$
$V_N = A + BP_{DNP}, \bar{P}_A = 0.89\%$	<i>n</i> -Nonane	$1.4 \pm 0.1$	$255 \pm 5$
	Ethylbenzene	$1.4 \pm 0.2$	$320 \pm 10$

\* Calculated according to Doerffel<sup>12</sup>.

TABLE III

HYDROCARBON DISTRIBUTION COEFFICIENTS FOR SORBENTS CONTAINING DMBA VERMICULITE AND DNP AT 84° (cm<sup>3</sup>/g)

Compound	$P_A = 0,$ $P_{DNP} = 0$	$A + BP_A,$ $P_{DNP} = 0$		$A + BP_{DNP},$ $P_A = 0$	$A + BP_{DNP},$ $\bar{P}_A = 0.89\%$		$K_A^*$
	$K_{GS}$	$K_{GS}$	$K_{GA}$	$\approx$	$K_{DNP}$	$K_{DNP}$	
Cyclohexane	0.15	0.10	14	0.0	44	43	6
<i>n</i> -Nonane	0.75	0.60	90	0.3	290	255	30
<i>n</i> -Decane	1.30	1.20	210	0.6	600	565	60
Benzene	0.35	0.40	95	0.0	69	61	21
Toluene	0.35	0.45	150	0.2	165	140	28
Ethylbenzene	0.95	1.00	230	0.2	355	320	33
<i>p</i> -Xylene	0.80	1.10	240	0.2	365	350	35
<i>m</i> -Xylene	0.95	1.10	380	0.2	375	350	45
<i>o</i> -Xylene	0.95	1.70	360	0.3	445	440	55
Cumene	1.20	1.50	290	0.2	540	495	35

\*  $K_A$  was determined separately.

The parameters of the dependences  $V_N = A_L + B_L P_{(A,L)}$  were calculated by the least-squares method. The results and the precision are given in Table II, using *n*-nonane and ethylbenzene as examples. Table III shows the distribution coefficients for all of the hydrocarbons analyzed in the system DMBA vermiculite-DNP.

It can be seen from Table II that  $A_L$  and  $B_L$  were determined with satisfactory accuracy, except for the case when  $\approx$  is small.

When sorbents that contain an organo-clay are used, the retention value may be considered to be the sum of contributions from the following processes: adsorption on the gas-solid support, gas-organoclay, SLP-organoclay, gas-SLP and SLP-solid support interfaces (in this work, the last two effects were not determined separately) and dissolution in the SLP layer. Such a conclusion follows from the significance of the distribution coefficients given in Table III.

The  $K_{GS}$  values determined on a solid support covered with an organo-clay and without an organo-clay are similar. This indicates that an organo-clay does not prevent adsorption on the surface of a solid support. The addition of an SLP to a solid support decreases the contribution of the adsorption to the retention value ( $K_{GS} > \approx$ ). It thus follows that an organo-clay, unlike an SLP, does not modify a solid support and the application of adsorption-active solid supports, especially at a low organo-clay content, is inefficient.

An approximate calculation by eqns. 3 and 4, using the data from Table III, shows that the adsorption contributions  $K_{GS}$  and  $\approx$  can be neglected when  $P_A > 7-10$  wt. % and  $P_L > 2-5$  wt. %.

The values of  $K_L$  determined in the presence of an organo-clay differ from those for an SLP without an organo-clay, indicating that the solubility in an SLP layer also changes in the presence of an organo-clay.

The role played by adsorption on an organo-clay surface decreases sharply upon addition of an SLP ( $K_{GA} > K_A$ ). This decrease is different for different compounds: 3.1-fold for *n*-nonane, 4.6-fold for benzene and 8.4-fold for cumene.

The results for the DMBA vermiculite-DBT system confirm the above trends (with a few exceptions) and are not given in this paper.

On the basis of the results, we can conclude that the net retention volume calculated per solid support mass depends linearly on the organo-clay and SLP contents (over the range investigated). However, a change in the distribution coefficients in the packing constituents as a result of the mutual effects of the constituents must be taken into account for all of the dissolution and adsorption processes considered.

It should be noted that the distribution coefficients for gas-SLP ( $K_L$ ) are higher than those for adsorption on organo-vermiculite ( $K_{GA}$  and  $K_A$ ), which indicates that an alteration of the SLP content changes the retention volume more than an alteration of the organo-vermiculite content.

Let us now consider the role of the dissolution and adsorption processes not in terms of absolute retention values but of separation selectivity for the chosen pairs of compounds. As shown by White<sup>5</sup>, organo-clays are selective for the separation of aromatic hydrocarbons from non-aromatic hydrocarbons and also for the separation of *meta*- from *para*-isomers of aromatic hydrocarbons. In order to characterize selectivity, it is advisable to choose pairs of compounds with similar boiling points. The role of specific effects is then more pronounced. Taramasso and Veniale<sup>6,7</sup> used the pairs benzene-cyclohexane and *m*-xylene-*p*-xylene to study the selectivity of organo-clays.

The characteristics of the retentions of cyclohexane, benzene and xylenes on sorbents containing organo-vermiculite and SLP were determined. The calculated ratios of the distribution coefficients for the above pairs of compounds on impregnated and non-impregnated organovermiculites ( $K_{GA, rel.}$  and  $K_{A, rel.}$ ) are given in Table IV.

TABLE IV  
RATIO OF DISTRIBUTION (ADSORPTION) COEFFICIENTS FOR THE SYSTEMS GAS-ORGANO-VERMICULITE AND GAS-(SLP-ORGANO-VERMICULITE INTERFACE)\*

<i>Sorbent</i>	<i>Temperature</i> (°C)	<i>Benzene-</i> <i>cyclohexane</i>	<i>m-Xylene-</i> <i>p-xylene</i>
DMBA vermiculite (Kovdor)	84	6.9	1.58
+ mineral oil	80	6.5	1.30
+ DIS	90	3.9	1.17
+ DNP	84	3.6	1.27
+ DBT	84	2.0	1.00
DMODA vermiculite (Kovdor)	91	9.6	1.75
- DIS	98	—	1.29
DMODA vermiculite (South Africa)	91	9.0	1.72
- DIS	59	10.0	1.50

\* The SLPs are arranged in order of increasing polarity

The results in Table IV show that the adsorption selectivity on the organo-clay surface decreases upon impregnation with SLP, the decrease being greater with an increase in the polarity of the SLP. A similar effect has been observed<sup>4</sup> for a sorbent containing Bentone 245 and mineral oil or DNP.

When a more polar SLP is used, such as dinitrochlorobenzene or triscyanethoxypropane, the organo-vermiculite selectivity decreases even more markedly, and when

the amount of SLP is sufficient the separation on a sorbent is determined mainly by the chromatographic properties of the SLP.

From Table IV, it also follows that the higher the selectivity of adsorption on the initial organo-vermiculite, the higher is the selectivity for the SLP-organovermiculite interface (DIS was used as the SLP).

The results have shown that the selectivity of the combined sorbent can be changed by adding various organo-clays. As the sorbent selectivity can be regulated not only by a change in adsorptive properties of the organo-clay (the modifying effect of the SLP) but also by dissolution in an SLP layer, the desirable selectivity of the sorbent as a whole can be obtained by impregnation of an organo-clay either with large amount of an SLP of low polarity or with a small amount of an SLP of higher polarity. These conclusions are of important practical interest and, in our opinion, increase the possible applications of organo-clays.

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