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ON THE MECHANISM OF SUPPORT SURFACE ADSORPTION IN GAS–LIQUID CHROMATOGRAPHIC SYSTEMS

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SUMMARY

The mechanism of support surface adsorption is investigated in gas–liquid chromatographic systems with supports exhibiting strong adsorptive properties. For this purpose the characteristic adsorption isotherm for solute adsorbed on the support is evaluated, using the theoretical method developed previously by the authors. This isotherm is then analyzed on the basis of the third-order interaction theory, which allows the determination of information on the mechanism of support surface adsorption.

INTRODUCTION

The adsorption effects in gas–liquid chromatographic systems have been investigated by many authors, and a great number of papers have been published in this field so far[1].

While some of the authors emphasized the role of liquid–gas interface adsorption, others demonstrated the predominant role of support surface adsorption. The main point is that in many GLC systems investigated in practice, one of the above-mentioned types of adsorption is negligible in comparison with the other. Strictly speaking, the contribution from one adsorption mechanism to the total retention volume is much greater than the contribution due to the second adsorption mechanism. Of course, the most general treatment of GLC systems should take into account the simultaneous occurrence of the two kinds of adsorption.

Such general treatment has recently been developed by CONDER *et al.*[2] and modified by SUPRYNOWICZ *et al.*[3].

On the one hand the simultaneous occurrence of the two kinds of adsorption may be a source of difficulty in some analytical cases and in theoretical considerations, but on the other hand it may be a source of quite new possibilities of both a practical and theoretical nature. Therefore, we are of the opinion that adsorption effects in GLC systems should not be eliminated at all, but rather modified, to a given analytical purpose. However, to be able to modify these adsorption effects, one must know in detail the mechanism of support surface and liquid surface adsorption.

From this point of view the liquid surface adsorption is a rather simple case. It is a typical physical adsorption on a highly uniform surface. However, complications appear when considering the mechanism of support surface adsorption.

It should be emphasized that even in the absence of liquid stationary phase the support surface adsorption is a complicated case, because of non-homogeneity and non-regularity of the support surface. The additional presence of liquid introduces some new difficulties, connected with the degree and mode of wetting of the support by the liquid.

The total support surface adsorption effect is assumed to consist of two parts, one due to the support–liquid interface adsorption and the other the support–gas interface adsorption.

In this paper we shall consider the GLC systems in which strong adsorptive forces exist between the solute molecules and the support surface. Strictly speaking, the potential energy of solute molecules adsorbed on the support surface is much greater than that in the liquid or adsorbed on the liquid surface. We shall present here a method for estimating the mechanism of support surface adsorption in this interesting case.

THEORY

Following many authors, we shall distinguish three sources of chromatographic processes: bulk liquid solution, support surface adsorption and gas–liquid interface adsorption. Accordingly, we consider the retention equation to be of the form:

$$V_N = V_l K_l + V_s K_s + V_i K_i \tag{1}$$

where V_N = the total retention volume, K_m is the partition coefficient in the mth retention mechanism ($m = l$, s or i) and V_m is the volume of zone where the mth retention mechanism takes place. The subscripts l, s, and i denote the bulk liquid partition, support surface adsorption, and liquid surface adsorption, respectively.

In the case of infinite dilution of solute eqn. 1 yields[3]

$$V_N^E = \sum_m V_m \exp\left[\frac{E_m}{-kT}\right],\ m = l, s, i \tag{2}$$

where E_m is the potential energy of a single molecule of solute in the zone V_m (the energy scale being chosen so that the potential energy in the free gas phase should be equal to zero). V_N^E is the retention volume, extrapolated to zero sample size of solute.

Now consider the problem of evaluating the parameters K_m, V_m which describe interactions in GLC systems. The parameter V_l is considered to be simply equal to the volume of the liquid stationary phase. Later, the parameter K_l can be easily obtained for both the case of infinite and finite dilutions of solute, for example from the plot of V_N/V_l against $1/V_l$, as recommended by CONDER[4].

Recently we have found the way to evaluate the parameters V_s, K_s, V_i, K_i, in the case of finite dilutions of solute, from chromatographic data alone[3]. For this one must find experimental values of the function $X(1/T)$, defined as follows:

$$X\left(\frac{1}{T}\right) = V_N^E - V_l K_l^E \tag{3}$$

where K_l^E is the bulk solution coefficient for infinite dilution of solute.

According to eqn. 2, the function $X(1/T)$ is assumed to have the following analytical form:

$$X\left(\frac{1}{T}\right) = V_s \exp\left[\frac{E_s}{-kT}\right] + V_i \exp\left[\frac{E_i}{-kT}\right] \tag{4}$$

Now, we choose values of the parameters V_s, E_s, V_i, E_i so that they should satisfy as closely as possible eqn. 4 with respect to experimental data from eqn. 3.

Suppose now that $E_s > E_l$ and $E_s > E_i$. Then, for a wide initial range of solute concentrations in the free gas phase, we can consider the densities in the zones V_l and V_i to be much smaller than the density in the zone V_s. Consequently, for this initial range of small solute concentrations, we can neglect mutual interactions between solute molecules in the zones V_l and V_i, whereas this cannot be done in the case of the zone V_s.

Thus, for this initial range of solute concentrations, eqn. 1 may be rewritten in the following form:

$$V_N = V_l \exp\left[\frac{E_l}{-kT}\right] + V_s K_s + V_i \exp\left[\frac{E_i}{-kT}\right] \tag{5}$$

From the above equation we can extract the part of the retention volume $V_{N,s}$ which is due to the solid support adsorption. Strictly speaking, the solid support adsorption is an average of two separate parts: support–gas interface adsorption and support–liquid interface adsorption[5].

Before continuing further, we need to discuss the concepts of the "support–gas" and the "support–liquid" interfaces. We consider the support–gas interface as that part of support surface where the adsorption of solute molecules is not affected by liquid molecules. Later, we shall consider the support–liquid interface as that part of the support surface where the adsorption of solute is affected by liquid, independent of whether or not the support surface is immediately struck by liquid molecules.

It has been shown earlier[6] that there exists a simple relation between the retention volume V_N and the concentration ρ_0 of solute in the free gas phase. In the case of the retention volume $V_{N,s}$ this relation yields

$$V_{N,s} = \sum_{i=2}^{\infty} B_{is} \rho_0^{(i-2)} \tag{6}$$

where B_{is} is the so-called i-th gas–solid virial coefficient. Thus, having $V_{N,s} = V_{N,s}(\rho_0)$, we easily obtain the adsorption isotherm for the solid support adsorption[7]

$$N_s = \rho_0 V_{N,s} \tag{7}$$

where N_s is the number of solute molecules adsorbed in the zone V_s.

The function $V_{N,s} = V_{N,s}(\rho_0)$ can be obtained from simple chromatographic data. For this purpose one must find the function $V_{N,s}(\rho_0)$ for a number of low concentrations, ρ_0. Next, by extracting from it the value

$$\left\{V_l \exp\left[\frac{E_l}{-kT}\right] + V_i \exp\left[\frac{E_i}{-kT}\right]\right\}$$

one obtains an approximate form of $N_s(\rho_0)$ by using eqn. 7. A more accurate form of this function can be obtained by extracting the value

$$\left\{V_l K_l(\rho_0) + V_l \exp\left[\frac{E_l}{-kT}\right]\right\}$$

with the value $K_l = K_l(\rho_0)$, found experimentally, since the non-ideality of the bulk liquid solution is then taken into account. The second procedure was used in our calculations.

In this way we obtain the adsorption isotherm for the support surface adsorption in the presence of liquid stationary phase.

It is well known that in eqn. 7 only the first two terms play any considerable role when expanding $V_{N,s}$ into the power series of density ρ_0, according to eqn. 6. These are the terms that include the second, B_{2s}, and the third, B_{3s}, gas–solid virial coefficients. The coefficients B_{2s} and B_{3s} may be written in the following form

$$B_{2s} = \int_V \left\{\exp\left[\frac{W_1(\boldsymbol{r}_1)}{-kT}\right] - 1\right\} \mathrm{d}\boldsymbol{r}_1 \tag{8}$$

$$\begin{aligned} B_{3s} = {} & \int_V \int \left\{\exp\left[\frac{W_1(\boldsymbol{r}_1) + W_1(\boldsymbol{r}_2)}{-kT}\right]\right\} \left\{\exp\left[\frac{\omega_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{-kT}\right] - 1\right\} \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \\ & - \int_V \int \left\{\exp\left[\frac{U_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{-kT}\right] - 1\right\} \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \end{aligned} \tag{9}$$

where V is the volume of the adsorption space, $W_1(\boldsymbol{r}_1)$ is the adsorption potential of a single molecule, whose centre is at the point $\boldsymbol{r}_1$; $\omega_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the interaction energy between two molecules in the presence of a solid; $U_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the interaction energy between two molecules in the free gas phase.

The difference between $\omega_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ and $U_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is connected with the presence of the so-called "third-order interaction" (two solute molecules plus surface) in the adsorbed phase.

From the theoretical calculations of SINANOGLU AND PITZER[8] it follows that the third-order interaction is a source of an additional repulsion between solute molecules when they are in a monolayer. If we assume $U_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ to be a Lennard-Jones type potential, *i.e.*,

$$U_2(\boldsymbol{r}_1,\boldsymbol{r}_2) = 4U_0 \left[\left(\frac{\delta}{r}\right)^{12} - \left(\frac{\delta}{r}\right)^{6}\right] \tag{10}$$

then $\omega_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ may be written in the form

$$\omega_2(\boldsymbol{r}_1,\boldsymbol{r}_2) = 4U_0 \left[\left(\frac{\delta}{r}\right)^{12} - \left(\frac{\delta}{r}\right)^{6} + \eta \left(\frac{\delta}{r}\right)^{3}\right] \tag{11}$$

where $r = (\boldsymbol{r}_1 - \boldsymbol{r}_2)$ is the distance between adsorbed molecules; U_0 is the depth of the potential minimum; δ is the slow-collision diameter and η is the proportionality constant.

Similar results have been obtained by YARIS[9] and by MCLACHLAN[10].

The repulsion effect in a monolayer, introduced by the additional term $\eta(\delta/r)^3$, amounts to about 20–40 % of the gas phase potential minimum, U_0. On the other hand, the same third-order interaction is a source of an additional attraction between adsorbed molecules if the two molecules are directly on top of one another, as in a multilayer formation. This additional attraction amounts to 10–20 % over the potential minimum, U_0.

FREEMAN[11] was the first to demonstrate the three-body effects in physical adsorption, whereas SAMS *et al.*[12] were the first to investigate these effects on the basis of the theoretical results of SINANOGLU AND PITZER[8]. More recent results are due to KRIZAN AND CROWELL[13], JOHNSON AND KLEIN[14] and WOLFE AND SAMS[15]. They still only consider two-dimensional models of adsorption, the differences between being only in their mode of evaluation of the third-order repulsion effect.

In the next section of our paper we shall show that discussion of three-body effects can be a source of information about the mechanism of support surface adsorption in the presence of a liquid stationary phase.

EXPERIMENTAL

In our illustrative measurements, we used Polsorb C, a support exhibiting strong adsorptive properties. This support was loaded with a liquid mixture of slightly polar dilauryl phthalate and polar fractonitrile III (3:1).

To find K_l, a number of different liquid loadings were investigated. These liquid loadings were 0.2 %, 0.4 %, 0.6 %, 0.8 %, 1.0 %, 3.0 %, 5.0 % and 10.0 % of mixed stationary phase by weight of Polsorb C, respectively.

Next, two chemically different substances (solutes), cyclohexane and carbon tetrachloride, were investigated. The retention data were measured at four temperatures, 65 °C, 80 °C, 100 °C and 120 °C. Each time five sample sizes (0.1 µl, 0.2 µl, 0.3 µl, 0.5 µl and 1.0 µl) of solute were introduced, by means of a Hamilton microsyringe. The concentrations of solutes obtained with these sample sizes varied from about 10^{-4} mole/l to about 10^{-3} mole/l.

The measurements were performed by means of the Polish apparatus, Chromatoprep N-502, with a catharometer as detector. The chromatographic column was 1 m in length and of 4 mm I.D. Hydrogen was used as the carrier gas, being cleaned additionally by 4A- and 5A-type molecular sieves.

RESULTS AND DISCUSSION

The results of the measurements and calculations are presented in Tables I–VI and in Figs. 1 and 2. In Tables I and II the total retention volumes are given for a number of different concentrations, ρ_0, at four temperatures. The values $X(1/T)$ used in the best-fit procedure are presented in Table III, whereas in Table IV the results of appropriate numerical calculations are given. By using the parameters from Table IV and experimental values of $V_l K_l$, the functions $V_{N,s}(\rho_0)$ were calculated, and are presented in Tables V and VI.

Now consider the shape of the adsorption isotherms, $N_s(\rho_0)$, in Figs. 1 and 2. According to the assumption that terms with ρ_0 powers higher than two are negligible, the shape of the isotherms should depend on whether B_{3s} is negative or positive.

TABLE I

RETENTION DATA FOR CYCLOHEXANE IN A GLC SYSTEM CONTAINING POLSORB C, COVERED BY 5% LIQUID (BY WEIGHT)

The mixture contains three parts of dilauryl phthalate and one part of fractonitrile III. Values of $V_{N_g} \cdot 10^3$ [a] are given in l/g; values of $\rho_0 \cdot 10^4$ in moles/l.

65 °C		*80 °C*		*100 °C*		*120 °C*	
$V_{N_g} \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_{N_g} \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_{N_g} \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_{N_g} \cdot 10^3$	$\rho_0 \cdot 10^4$
5.87	1.94	3.81	2.37	2.46	3.39	1.49	3.24
5.89	3.81	3.86	5.01	2.46	5.26	1.49	6.48
5.98	5.63	3.88	7.21	2.43	8.27	1.46	9.68
6.19	9.20	3.85	11.66	2.43	14.62	1.46	16.19
6.19	17.50	3.88	22.41	—	—	1.49	29.16

[a] V_{N_g} = absolute retention volume per gram of column packing.

TABLE II

RETENTION DATA FOR CARBON TETRACHLORIDE IN A GLC SYSTEM CONTAINING POLSORB C, COVERED BY 5% LIQUID (BY WEIGHT)

The mixture contains three parts of dilauryl phthalate and one part of fractonitrile III. Values given in units as in Table I.

65 °C		*80 °C*		*100 °C*		*120 °C*	
$V_{N_g} \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_{N_g} \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_{N_g} \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_{N_g} \cdot 10^3$	$\rho_0 \cdot 10^4$
7.18	1.76	4.58	2.41	2.92	2.98	1.84	3.37
7.29	3.44	4.58	4.79	2.89	5.71	1.81	6.39
7.40	5.61	4.58	7.20	2.89	8.15	1.78	10.31
7.40	7.40	4.43	11.20	2.92	13.37	1.76	15.92
7.51	16.70	4.58	21.24	—	—	1.71	28.33

TABLE III

EXPERIMENTAL VALUES OF THE FUNCTION $X(1/T)$ USED IN THE BEST-FIT PROCEDURE

Temperature (°C)	*Carbon tetrachloride*		*Cyclohexane*	
	X (1/T) (l/g)	K_l^E	*X (1/T) (l/g)*	K_l^E
65	$4.19 \cdot 10^{-3}$	125.46	$3.60 \cdot 10^{-3}$	97.13
80	$2.87 \cdot 10^{-3}$	85.18	$2.44 \cdot 10^{-3}$	69.97
100	$1.78 \cdot 10^{-3}$	53.57	$1.53 \cdot 10^{-3}$	44.30
120	$1.10 \cdot 10^{-3}$	31.47	$0.92 \cdot 10^{-3}$	26.01

TABLE IV

INTERACTION PARAMETERS OBTAINED FROM NUMERICAL CALCULATIONS

Solute	V_s *(cm³)*	E_s *(cal/mole)*	V_l *(cm³)*	E_l *(cal/mole)*	E_l *(cal/mole)*
Carbon tetrachloride	$0.82 \cdot 10^{-4}$	−4924	$0.23 \cdot 10^{-3}$	−3275	−3086
Cyclohexane	$0.80 \cdot 10^{-4}$	−5854	$0.28 \cdot 10^{-4}$	−3257	−3009

TABLE V

DATA USED IN CALCULATING THE ADSORPTION ISOTHERMS $N_s(\rho_0)$ FOR CYCLOHEXANE

Values given in units as in Table I.

65 °C		*80 °C*		*100 °C*		*120 °C*	
$V_sK_s \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_sK_s \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_sK_s \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_sK_s \cdot 10^3$	$\rho_0 \cdot 10^4$
1.03	1.94	0.28	2.37	0.19	3.39	0.14	3.24
1.06	3.81	0.34	5.01	0.20	5.26	0.14	6.48
1.14	5.63	0.34	7.21	0.16	8.27	0.11	9.68
1.35	9.20	0.36	11.66	0.16	14.62	0.11	16.19
1.36	17.50	0.36	22.41	—	—	0.14	29.16

TABLE VI

DATA USED IN CALCULATING THE ADSORPTION ISOTHERMS $N_s(\rho_0)$ FOR CARBON TETRACHLORIDE

Values given in units as in Table I.

65 °C		*80 °C*		*100 °C*		*120 °C*	
$V_sK_s \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_sK_s \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_sK_s \cdot 10^3$	$\rho_0 \cdot 10^4$	$V_sK_s \cdot 10^3$	$\rho_0 \cdot 10^4$
0.91	1.76	0.27	2.41	0.17	2.98	0.20	3.37
1.02	3.44	0.29	4.79	0.13	5.71	0.16	6.39
1.13	5.60	0.27	7.20	0.13	8.15	0.13	10.31
1.23	7.40	0.27	11.20	0.17	13.37	0.11	15.92
1.24	16.70	0.27	21.24	—	—	0.06	28.33

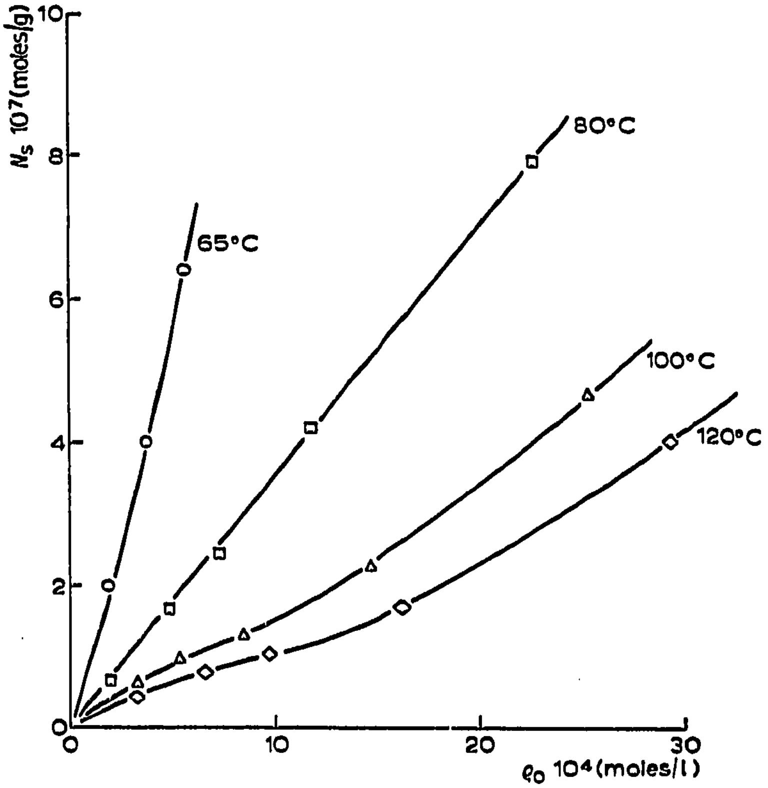

Fig. 1. The adsorption isotherms $N_s(\rho_0)$ for cyclohexane.

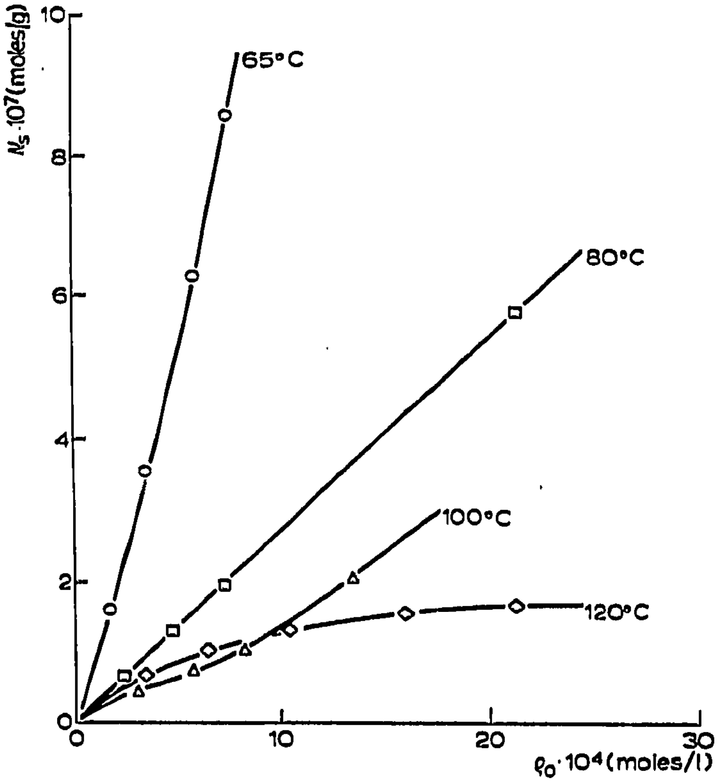

Fig. 2. The adsorption isotherms $N_s(\rho_0)$ for carbon tetrachloride.

In the case of a negative B_{3s} the adsorption isotherms should be of the first, second or fourth type, whereas in the case of a positive B_{3s} of the third or fifth type.

Both B_{2s} and B_{3s} are functions of temperature, being equal to zero for some temperatures, called by SAMS *et al.*[12] "first gas–surface characteristic temperature" and "second gas–solid characteristic temperature", respectively. These temperatures also depend upon the gas–solid interaction function, as well as upon the intermolecular interaction function.

It has been found by SAMS that the first gas–solid characteristic temperature for the (9–3) gas–solid interaction should be equal to 1417°K, and is therefore not accessible experimentally.

In the experimental conditions under investigation, B_{2s} is still positive. In contradiction to the first characteristic temperature, the second one is often found in practice. At this temperature the adsorption systems behave as ideal systems, in spite of intermolecular forces which do, in fact, exist. The adsorption isotherms are then linear functions of the adsorbate density, ρ_0.

Now, we would like to introduce some theoretical results obtained by SAMS *et al.*[12], which will be basis of later discussion.

Considering the two-dimensional model of adsorption, and assuming the adsorption forces between admolecules to be LJ (12–6) interactions, unperturbed by the presence of solid, SAMS *et al.*[12] found that the second gas–solid characteristic temperature should be equal to $3U_0/2k$. Possible deviations from this value may be due to deviations from the two-dimensional model or to the third-order interactions discussed above. There exists the additional possibility of perturbations due to the presence of liquid.

Thus, the experimental value of the second gas–solid characteristic temperature may be a source of interesting information about the adsorption mechanism.

Now, let us consider the adsorption isotherms in Figs. 1 and 2. It is seen from these figures that the second characteristic temperature for cyclohexane is close to the appropriate value for carbon tetrachloride. They are both approximately 80°C. From this it follows that the value U_0/k for these substances, adsorbed on the support surface in our GLC systems, should be equal to about 233°K.

This value can be compared with appropriate values for bulk phases. The bulk value U_0/k found by LAUGER[16] from the transport properties of liquid carbon tetrachloride is equal to 282°K. The value for cyclohexane found from the relation $U_0/k = 0.77T_c$ (semi-empirical relation found on the basis of LJ (12–6) interaction) is equal to 216°K[17]. Here T_c is the critical temperature.

Now suppose that the solutes form a monolayer on the surface of Polsorb C. Then the experimental values U_0/k, calculated on the basis of the third-order interaction theory, should vary in the intervals 169–215°K and 129–173°K, for carbon tetrachloride and cyclohexane, respectively (additional repulsion from about 20–40 %U_0). The additional presence of liquid should in the third-order approximation increase this tendency, and hence lead to smaller values of U_0/k for the adsorbed phase.

It can be seen that the theoretical value of U_0/k for adsorbed carbon tetrachloride, *i.e.* 233°K, is very close to the theoretical value 215°K, calculated with the assumptions of monolayer formation and the smallest possible third-order repulsion effects (assuming the presence of one perturbing body only). The absence of a second perturbing body means here the absence of a liquid phase. From this it follows that the adsorption of CCl_4 on Polsorb C takes place on the parts of support surface which are not covered by liquid phase. The monolayer formation is now predominant, since multilayer formation would increase U_0/k (additional third-order attraction).

On the other hand, in the case of cyclohexane, the assumption of monolayer formation leads to a considerable discrepancy between the experimental, *i.e.* 233°K, and the theoretical data, *i.e.* 173°K, even with the smallest possible perturbations in the monolayer. The experimental value is even higher than the value for the bulk phase, *i.e.* 216°K. This is evidence of a great contribution from additional third-order attraction forces, and therefore of extensive multilayer formation. The highest layers may be additionally perturbed by the nearest liquid molecules, which should increase the experimental value U_0/k a little more. In fact, this value is relatively very high.

Thus, in contradiction to carbon tetrachloride, the adsorption of cyclohexane on Polsorb C in our GLC system should be of multilayer character, with strong intermolecular interactions, when solute molecules are directly on top of one another.

It should be noted that theoretical concepts connected with the presence of the three-body effects allow for many other interesting investigations. However, they require extremely accurate measurements, which may be performed easily only in pure gas–solid systems. The experimental isotherms $N_s(p_0)$ were obtained indirectly by us, and we are not sure that we can draw more precise conclusions.

Therefore, we have confined ourselves to these general conclusions about the mechanism of support surface adsorption in our GLC systems.

REFERENCES

1 C. Eon, A. K. Chatterjee and B. L. Karger, *Chromatographia*, 5 (1972) 28.
2 J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 700.
3 Z. Suprynowicz, A. Waksmundzki and W. Rudziński, *J. Chromatogr.*, 67 (1972) 21.
4 J. R. Conder, *J. Chromatogr.*, 39 (1969) 273.
5 J. C. Giddings, *Anal. Chem.*, 35 (1963) 440.
6 W. Rudziński, Z. Suprynowicz and J. Rayss, *J. Chromatogr.*, 66 (1972) 1.
7 R. A. Pierotti, *Chem. Phys Lett.*, 2 (1968) 385
8 O. Sinanoglu and K. S. Pitzer, *J. Chem. Phys.*, 32 (1960) 1279.
9 R. Yaris, *Thesis*, University of Washington, Seattle, 1962.
10 A. D. McLachlan, *Mol. Phys.*, 7 (1964) 381.
11 M. P. Freeman, *J. Phys. Chem.*, 62 (1958) 729.
12 J. R. Sams, G. Constabaris and G. D. Halsey, *J. Chem. Phys.*, 36 (1962) 1334.
13 J. E. Krizan and A. D. Crowell, *J. Chem. Phys.*, 41 (1964) 1332.
14 J. D. Johnson and M. L. Klein, *Trans. Faraday Soc.*, 60 (1964) 1964.
15 R. Wolfe and J. R. Sams, *J. Chem. Phys.*, 44 (1966) 2181.
16 P. Lauger, *Helv. Chim. Acta*, 45 (1962) 1109.
17 J. O. Hirschfelder, C. F. Curtis and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.