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INFLUENCE OF SILANIZATION ON ADSORPTIVE PROPERTIES OF SUPPORTS IN GAS-LIQUID PARTITION CHROMATOGRAPHY

Z. SUPRYNOWICZ, A. WAKSMUNDZKI AND W. RUDZIŃSKI
Department of Physical Chemistry, Institute of Chemistry UMCS, Lublin, Nowotki 12 (Poland)

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SUMMARY

Changes in the mechanism of support-surface adsorption in gas-liquid partition chromatography systems, due to silanization of support surface, are investigated. Some parameters describing support-surface adsorption have been evaluated for appropiate gas-liquid partition chromatography systems before and after silanization. The study was carried out by using the "best-fit" procedure, presented earlier by the authors.

INTRODUCTION

Recently, we published a paper[1] that described the first method of evaluating quantitatively the contributions of the three retention mechanisms — bulk liquid partition, support surface adsorption and liquid surface adsorption — that contribute to the total retention volume, which involved chromatography alone. This is a mathematical procedure based on numerical calculations, but experimental data that are required can be simply obtained by gas chromatography. These are the retention volumes, measured at several temperatures, and then extrapolated to zero sample size of the solute.

One obtains by using this procedure five parameters, which fully describe the quantitative adsorptive properties of gas-liquid partition chromatography (GLPC) systems.

The problem of particular interest is the investigation of the adsorptive properties of the support-liquid interface in the presence of the liquid phase. Many studies have been carried out in this field, and have recently been discussed in detail by CONDER *et al.*[2].

One of the most interesting aspects is the investigation of the changes in the adsorptive properties of supports due to the silanization processes.

Chromatographic supports often exhibit strong adsorptive and catalytic properties[3-5], which may be a source of difficulties in many analytical problems. Moreover, theoretical investigations involving chromatographic data may be difficult because of the above effects. Therefore, many attempts have been made to decrease the strong specific effects as far as possible, and have been discussed in detail by LEIBNITZ AND STRUPPE[6]. One of the most effective methods is the silanization of solid support surfaces.

In the silanization process, the "active" centres (siloxyl groups, active hydrogen ions) react with silanizating reagents to form trimethylsilane groups, being a type of organosilicon thin films. Such films do not interact with solute molecules, or only to a small extent[7,8]. For this reason, silanized supports are often used as standards in comparison with which the adsorptive properties of other supports are determined. These standards[8–11] are assumed to be non-interacting, especially when some physico-chemical quantities are being calculated, as, for example, partition coefficients or excess molar heats of solution[11,12].

The silanizing reagents most often used are HDMCS[13], DMCS and TMCS[14,15]. KIRKLAND[16] found that DMCS is the most effective reagent. It was shown that treatment of supports with HCl before silanization makes the silanization more effective.

Recently, mixtures of several silanizing reagents have been used, *e.g.*, Silyl 8, produced by Pierce Chemical Co. Sylil 8 can be simply introduced into chromatographic columns by means of a microsyringe.

The effectiveness of silanization depends not only on the reagent used, but also on the way in which the silanization is carried out (static methods of sorption from organic solvents, or dynamic methods of treating the supports by reagent vapour immediately in chromatographic columns[17,18]). In addition, radioactive radiation has been used to make silanization more effective[19].

It is generally assumed that the adsorptive properties of silanized support surfaces differ extremely from those that existed before the silanization and supporting experimental results have been reported by many investigators[8–12,20,21]. However, no method existed for fully evaluating the quantitative changes in adsorptive properties of supports as a result of silanization processes. We feel that our method for the quantitative description of adsorption phenomena in GLPC systems[1] should be very useful for this purpose.

THEORETICAL

The theoretical problems of our method have been described in detail in a previous paper[1]. In this paper we present and discuss only some basic results that are required for the understanding of the application of the method.

As in the previous paper, we consider the case of infinite dilutions of solute. This ideal case is a good approximation in conventional elution chromatography, in which the concentrations of solutes are very small (sample size *ca.* 0.1 μl). Next, we assume that the total retention volume, V_N, consists of three parts, resulting from the three retention mechanisms: bulk liquid partition, support–liquid interface adsorption and gas–liquid interface adsorption. Accordingly

$$V_N = K_l V_l + K_s V_s + K_i V_i \qquad (1)$$

where K_l, K_s and K_i are the partition coefficients for bulk liquid solution, support surface adsorption, and liquid surface adsorption, respectively, and V_l, V_s and V_i are the volumes of the zones in which the above retention mechanisms take place.

In the case of infinite dilution of solute, the mutual interactions between the solute molecules can be neglected. Then, from statistical thermodynamics, there exist simple relationships between the partition coefficients K_m $(m = l, s, i)$, and the potential energies, E_m, of the solute molecules in the zones V_m:

$$K_m = \exp\left(\frac{E_m}{-kT}\right) \tag{2}$$

where k is the Boltzmann constant and T is the absolute temperature.

From eqns. 1 and 2,

$$V_N = \sum_m V_m \exp\left(\frac{E_m}{-kT}\right) \tag{3}$$

It is well known that K_l and V_l can be found experimentally. V_l is assumed to be equal to the volume of the liquid phase, and K_l can be found from the plot $V_N = V_N(V_l)$, at higher degrees of coverages of the support by liquid. Now, let the value of $X\left(\frac{1}{T}\right)$ defined by

$$X\left(\frac{1}{T}\right) = V_N - K_l V_l \tag{4}$$

or

$$X\left(\frac{1}{T}\right) = V_s \exp\left(\frac{E_s}{-kT}\right) + V_l \exp\left(\frac{E_l}{-kT}\right) \tag{5}$$

be known for a number (at least four) of temperatures. The parameters V_s, E_s, V_t and E_t are chosen so that they approximate as accurately as possible to the experimental plot of $X\left(\frac{1}{T}\right)$ from eqn. 4 when it is assumed to have the analytical form given in eqn 5.

By using the best-fit procedure, two pairs of values of V,E are obtained. The problem that remains is to ascribe these pairs to appropriate types of adsorption phenomena. Some additional tests must therefore be carried out so as to be able to assign some pair to adsorption by the support or by the liquid surface. These tests may be of either an experimental or theoretical nature. The method of identification depends on the GLPC system under investigation, and, above all, on the inventiveness of the investigator.

We are of the opinion that the parameters V_s and E_s are very useful for characterizing the adsorptive properties of supports. Their changes after silanization can be regarded as being a quantitative measure of the changes resulting from the silanization.

Of course, the change in the adsorptive properties of a support should affect to some extent both the parameter E_l and the parameters E_t, V_t, because of the long-range interactions that may exist. On the other hand, it is obvious that the extent of the changes in E_l should be smaller than those in E_s, and much smaller in V_t, E_t. The last conclusion can be treated as a kind of test in the identification problem discussed above. It can be assumed that two pairs, V_1, E_1 and V_2, E_2, taken from appropriate (the most similar) sets of pairs before and after silanization are the pairs that are related to adsorption on the liquid surface. This test has been used by us in the identification of the pairs obtained in numerical calculations.

The best-fit procedure applied here requires numerical calculations, but in our opinion there is no difficulty in using it nowadays.

EXPERIMENTAL

The measurements were carried out under conditions very similar to those applied in our previous work. The purpose was to compare results obtained by using pure and silanized diatomite D.

As the support we used the silanized diatomite D "Polsorb C", with a specific area of 2.02 m^2/g and a particle diameter in the range 0.1–0.3 mm. This solid was covered with dinonyl phthalate from an ethereal solution by using the dynamic method. In this manner three GLPC systems were obtained, containing 1, 2 and 5 % (w/w) of the liquid, respectively.

Further, two substances, cyclohexane and carbon tetrachloride, were examined. In each instance a 0.1-μl volume of the solute was introduced by means of a Hamilton microsyringe.

Hydrogen was used as the carrier gas purified by use of type 5A molecular sieve. The flow-rate was about 75 ml/min.

The pressure gradient, expressed as the ratio of the pressure before the column to the atmospheric pressure, was about 1.5.

Reagents

Dinonyl phthalate, 99 %, produced by BDH (Great Britain).

Cyclohexane, produced by POCh Gliwice (Poland), re-distilled, and purified with type 5A molecular sieve.

Carbon tetrachloride, produced by POCh Gliwice (Poland), re-distilled, and purified with type 5A molecular sieve.

RESULTS AND DISCUSSION

The results of our measurements and calculations are presented in Tables I and II, respectively. In addition to the results for silanized Polsorb C, the analogous results for non-silanized Polsorb C are also given for the purpose of comparison.

TABLE I

EXPERIMENTAL RESULTS

$X\left(\frac{1}{T}\right)$	*Cyclohexane*					*Carbon tetrachloride*				
(cm^3)	50°	65°	80°	100°	120°	50°	65°	80°	100°	120°
Before silanization	2.05	1.16	0.75	0.44	0.24	2.32	1.36	0.84	0.46	0.27
After silanization	4.61	3.09	2.10	1.34	0.84	6.33	5.10	2.79	1.73	1.07

Before considering our findings the results for non-silanized Polsorb C which were presented in our previous paper should be mentioned[1], but in another form. The difference lies in the fact that the pair $E = 8887$, $V = 1.44 \cdot 10^{-6}$ (carbon tetrachloride) was previously ascribed to the gas–liquid interface adsorption, whereas the second computed pair was ascribed to the support–liquid interface adsorption. We

TABLE II

RESULTS OBTAINED FROM CALCULATIONS

Compound	*Bulk liquid partition*	*Support surface adsorption*		*Gas–liquid surface adsorption*	
	E_l (*cal/mole*)	E_s (*cal/mole*)	V_s (*cm*^{3})	E_t (*cal/mole*)	V_t (*cm*^{3})
Cyclohexane					
Before silanization	2969	7191	$1.52 \cdot 10^{-5}$	3807	$1.80 \cdot 10^{-4}$
After silanization	2705	14789	$1.82 \cdot 10^{-9}$	3083	$3.35 \cdot 10^{-4}$
Carbon tetrachloride					
Before silanization	3132	8887	$1.44 \cdot 10^{-5}$	3888	$5.6 \cdot 10^{-5}$
After silanization	2792	18429	$1.51 \cdot 10^{-11}$	3344	$2.21 \cdot 10^{-4}$

made this identification on the basis of similarity between the values E_s before and after covering the support with liquid. We now feel that the present investigations do not give support to the above identification.

We now feel that the most appropriate and reliable test is the similarity of gas–liquid adsorption effects before and after silanization. This type of test has been accepted in this paper, and such identifications allow for a simple interpretation of the experimental results reported here.

Let us begin with a discussion of solid support adsorption. It was generally assumed[2,8,22] that the support surface adsorption is an average effect, which consists of two separate effects, support–liquid interface adsorption and support–gas interface adsorption. In our opinion, the results in Table II provide evidence that support–gas interface adsorption is a predominant component of the total support surface adsorption, when using silanized supports (at least for Polsorb C). This follows from the following explanation of the results given in Table II.

Polsorb C is a type of silica gel with a non-uniform solid surface. The most active adsorption regions are crystal edges and narrow pores. Silanization reduces the strongly adsorptive activity of the surface, although to different extents on the wide planar parts of the surface and in narrow pores. In the narrow pores, the silanization is considerably enhanced because of steric effects.

Hence there remains after silanization a small volume (in the narrow pores) in which strong adsorptive forces exist, whereas on wide planar parts of the surface the adsorption is virtually negligible.

As shown earlier[20] silanization causes support surfaces to exhibit hydrophobic properties, although on the other hand it prevents wetting of supports by liquids in narrow pores (a pore-size distribution analysis showed that there exists a maximum in the distribution curve near 45Å[23]; in this case, the narrow pores are not wetted, and decide the form of the support surface adsorption. The support surface adsorption will be, in this case, of the support–gas interface type, exhibiting high adsorption energies (E_s) and a small volume of the zone in which such adsorption takes place (the volume of the narrow pores).

The last conclusions are in excellent agreement with our experimental results. It can be seen from Table II that for both cyclohexane and carbon tetrachloride the E_s values are very high for silanized Polsorb C. On the other hand, the V_s values are exceptionally small.

For non-silanized Polsorb C, one would expect good wetting of supports by liquids, which may be the origin of the two following effects. Firstly, there originates a new type of interface, *viz.* a support–liquid interface, its properties being determined predominantly by the solid–liquid interactions. Secondly, these interactions have the additional effect of "blocking" the most active centres, even in narrow pores, as they are then available for liquid.

Of course, in addition to the predominant part of the short-range Van der Waals forces, there may exist long-range induced forces, which can modify not only the bulk liquid partition, but also the liquid–gas interface adsorption. Because of the lack of symmetry of the long-range forces, they should increase the energies E_l and E_t, which can be seen in Table II. In fact, both E_l and E_t are even higher for non-silanized Polsorb C for both cyclohexane and carbon tetrachloride.

The following problem, of a mathematical nature, should be mentioned. One of our basic theoretical assumptions was the temperature independence of the parameters E_l, E_s, E_t, V_s and V_t, which is in fact not strictly true. For instance, the degree of support wetting changes with changes in temperature. This has, of course, a considerable influence on the above parameters. Therefore, the parameters evaluated are values averaged over the temperature range of the measurements. However, these difficulties can be avoided simply by decreasing the temperature range as much as possible, but this requires an even greater increase in the accuracy of the measurements.

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