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INVESTIGATIONS OF ADSORBENT HETEROGENEITY BY GAS CHROMATOGRAPHY

I. INVESTIGATION OF ADSORPTION MECHANISM ON HETEROGENEOUS SURFACES

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SUMMARY

The new graphical method for investigating adsorption mechanisms on heterogeneous surfaces, developed recently by Rudziński, Tóth and Jaroniec, is applied to gas chromatographic data. It is shown that the function $(\partial \ln p/\partial \ln N_t)$, giving the adsorption mechanism, can easily be evaluated from the function $V_N = V_N(p)$, obtained directly from gas chromatographic measurements. Moreover, the use of the function $V_N(p)$ in the evaluation of $(\partial \ln p/\partial \ln N_t)$ gives a smaller error than the use of the adsorption isotherm. The utilisation of gas chromatographic data is demonstrated for four adsorption systems, obtained by using two silica gels and two adsorbates.

INTRODUCTION

In recent investigations of physical adsorption, a problem of great importance and interest is the influence of adsorbent heterogeneity on the adsorptive properties of adsorption systems. The problem is to evaluate the distribution of adsorption energy and to estimate the adsorption mechanism.

Nine years ago Prof. Everett said: "We still have a long way to go in understanding adsorption by heterogeneous surfaces."[1] Many well-known scientists[2–5] working in the field of physical adsorption have devoted papers to this problem, but "The problem of heterogeneity is still one of the great unresolved problems of physical adsorption" wrote Prof. Pierotti last year[6]. From the results obtained so far, it follows that the effects of heterogeneity are greater than previously supposed.

Several models and procedures have been proposed[2–4,7–9] in order to investigate heterogeneity effects in adsorption. The most widely known and most often used procedure is to consider the whole surface to consist of small areas, within which adsorption is homogeneous, but between which adsorption varies. The overall (total) adsorption isotherm $N_t(p,T)$ is then assumed to be of the form[10]

$$N_t(p,T) = \int_0^\infty x(\varepsilon)\cdot N_1(\varepsilon,p,T)\mathrm{d}\varepsilon \tag{1}$$

where $x(\varepsilon)$ is the distribution of adsorption energy, and $N_1(\varepsilon,p,T)$ is the "local" adsorption isotherm that governs adsorption within the small area having adsorption energy equal to ε.

By solving eqn. 1 with respect to the function $x(\varepsilon)$, one derives the quantitative description of the energetic heterogeneity of the adsorbent for a given adsorption system. This problem will be discussed in the second part of the paper.

However, apart from difficulties connected with the evaluation of $x(\varepsilon)$, this function does not provide any information about the adsorption mechanism on heterogeneous surfaces. Such information may be obtained using the graphical method developed recently by Rudziński *et al.*[11]. The purpose of this paper is to present the possible application of some simple chromatographic data to the above-mentioned graphical method. It will be shown that the chromatographic data are more appropriate and easy to use in this graphical method than classical adsorption measurements (isotherms).

THEORETICAL

One of the simplest approximations of $x(\varepsilon)$ is the assumption that the adsorbent surface is patchwise, *i.e.*

$$x(\varepsilon) = \sum_{i=1}^{r} N_i^0\delta(\varepsilon-\varepsilon_i) \tag{2}$$

where N_i^0 is the number of adsorption sites having an adsorptive energy equal to ε_i and $\delta(\varepsilon-\varepsilon_i)$ is the delta function. Further, r is the number of distinct adsorption areas existing on the adsorbent surface. With this assumption Hill[12] has theoretically investigated the complicated but very interesting case of multilayer adsorption on heterogeneous surfaces when, in addition, the number of sites available for secondary adsorption, D^0, is different from the number of sites available for primary adsorption. The overall (total) adsorption isotherm N_t then has the form,

$$N_t(p,T) = \sum_{i=1}^{r}\left(\frac{N_i^0 p}{b_i+p}\right) - \frac{D^0 p}{b_s-p} \tag{3}$$

where

$$b_i = Q_{ip}^{-1}\exp\left(\frac{\mu_0+\varepsilon_i}{RT}\right) \text{and } b_s = Q_s^{-1}\exp\left(\frac{\mu_0+\varepsilon_s}{RT}\right)$$

μ_0 = standard chemical potential
Q_{ip} = internal molecular partition function of the primarily adsorbed molecules
ε_s = adsorption energy of the secondarily adsorbed molecules
Q_s = internal molecular partition function of the secondarily adsorbed molecules.

The second term in eqn. 3, like the Langmuir equation, describes the effect of the secondary (multilayer) adsorption.

However, the assumption expressed in eqn. 2 seems to be a very approximate one. It means that all adsorption sites within an area are identical, which is of course unrealistic.

Recently Rudziński *et al.*[11] have extended the above theoretical treatment to consider the small areas as groups of similar adsorption sites. They also assumed the secondary adsorption on each area to be specific and to obey the same assumptions made for primary adsorption.

In particular, they also assumed heterogeneity within every area for the secondary adsorption. With these assumptions, eqn. 3 yields

$$N_t(p,T) = \sum_{i=1}^{r}{}_r[N_{ip}(p,T)+N_{is}(p,T)] \tag{4}$$

where N_{ip} and N_{is} are the local adsorption isotherms describing the primary and secondary adsorptions on the *i*-th area of surface, respectively.

The theory of Rudziński *et al.*[11] was given in the form of a short letter. We shall discuss here some additional details which will be necessary in the analysis of the experimental data.

If we assume the existence of heterogeneity for the primary and secondary characteristic adsorptions, then N_{ip} and N_{is} are in fact integrals of the type given by eqn. 1

$$N_{ip}(p,T) = \int_0^\infty x_{ip}(\varepsilon) N_{uip}(\varepsilon,p\ T)\,\mathrm{d}\varepsilon \tag{5}$$

$$N_{is}(p,T) = \int_0^\infty x_{is}(\varepsilon) N_{uis}(\varepsilon,p,T)\,\mathrm{d}\varepsilon \tag{6}$$

where x_{ip} and x_{is} are the appropriate energy distributions within the *i*-th area of the surface for the primary and secondary adsorptions, respectively. Further, N_{uip} and N_{uis} are the "ultralocal" adsorption isotherms, governing adsorption on the sub-areas of the *i*-th area, having an adsorption energy equal to ε.

One of the most investigated energy distributions is the exponential energy distribution

$$x(\varepsilon) = \frac{\sin \pi C}{\pi RT}\left[\exp\left(\frac{\varepsilon}{RT}\right) - 1\right]^{-C} \tag{7}$$

Assuming further that the ultralocal adsorption isotherms N_{uip} and N_{uis} are the Langmuir terms appearing in eqn. 3, *i.e.*

$$N_{uix}(\varepsilon,p,T) = \left[1 + \frac{d_{ix} sgn(x)}{p}\exp\left(\frac{-\varepsilon}{RT}\right)\right]^{-1} \tag{8}$$

where

$$d_{ix} = Q_{ix}{}^{-1}\exp\left(\frac{\mu_0}{RT}\right) \tag{9}$$

and

$$sgn(x) = \begin{cases} +1 & \text{for } x=p \\ -1 & \text{for } x=s \end{cases} \tag{10}$$

With these assumptions we obtain

$$N_{ip} = \left[\frac{p}{p+d_{ip}}\right]^{C_{ip}} \tag{11}$$

$$N_{is} = \left[\frac{p}{p-\mathrm{d}_{is}}\right]^{C_{is}} \tag{12}$$

In eqns. 11 and 12 the constants C_{ip} and C_{is} are the heterogeneity parameters, describing the local heterogeneity within the i-th area for primary and secondary adsorptions, respectively.

The last assumption introduced by Rudziński *et al.* was that the overall adsorption process ideally is stepwise, *i.e.*, at a given pressure only one local characteristic adsorption actually occurs. Harris[13, 14] pointed out that the assumption of the stepwise character of adsorption is a good working approximation when calculating the thermodynamic properties of adsorption systems. This assumption means that at every pressure the overall adsorption process may be described by the following equation

$$N_t(p,T) = \text{Const.} + \left[\frac{p}{p+d_{ix}sgn(x)}\right]^{C_{ix}} \tag{13}$$

The results from eqns. 11 and 12 have been obtained using the method of Stieltjes' transform, first introduced by Sips[7].

Eqn. 3 may be written in the following differential form

$$\frac{\partial \ln p}{\partial \ln N_t} = \frac{p \cdot sgn(x)}{d_{ix} \cdot C_{ix}} + \frac{1}{C_{ix}} + C_{ix} \tag{14}$$

In fact, C_{ix} is a slowly varying function of pressure, as $C_{ix} = (\partial N_t/\partial p) \cdot (p/N_{ix})$, where N_{ix} is the amount of solute adsorbed at the pressure at which the ix-th characteristic local adsorption starts. Of course for the first characteristic local adsorption $C_{1p} = 0$. Note that the function C_{ix} is a slowly varying one, as $(\partial N_t/\partial p) \cdot (p/N_{ix})$ is simply the ratio of the actual derivate of the adsorption isotherm to the tangent of the subtense joining the zero-pressure point to the point on the isotherm where the ix-th characteristic adsorption starts. For this reason we treat C as constant in a pressure region, corresponding to some characteristic local adsorption. From eqn. 14 it follows that the plot of $(\partial \ln p/\partial \ln N_t)$ against (p) should consist of a number of linear parts, from which the parts having positive slopes (tangent values) relate to specific primary adsorptions, whereas the parts with negative slopes relate to specific secondary adsorptions.

Concluding from the above results, the function $(\partial \ln p/\partial \ln N_t)$ is an approximate diagram of adsorbent heterogeneity and an excellent diagram of adsorption mechanism.

Consider now how gas chromatographic data can be used to evaluate the function $(\partial \ln p/\partial \ln N_t)$. To this purpose note that the basic law of gas elution chromatography may be expressed as[15]

$$V_N = F\frac{\partial N_t}{\partial \rho_0} \tag{15}$$

where V_N is the retention volume, ρ_0 is the adsorbate density in the free gas phase and F is the James–Martin compressibility factor.

It is well known that in the case of typical adsorption systems the adsorbate in the bulk (free gas) phase may be considered as ideal in a large region of bulk adsorbate pressures. With this assumption, we obtain

$$V_N = FRT\frac{\partial N_t}{\partial p} \tag{16}$$

$$N_t(\rho_0) = \frac{1}{F}\int_0^{\rho_0} V_N(\rho_0)\mathrm{d}\rho_0 \tag{17}$$

$$N_t(p) = \frac{1}{FRT}\int_0^{p} V_N(p)\mathrm{d}p \tag{18}$$

From eqns. 15–18 we obtain

$$\frac{\partial \ln p}{\partial \ln N_t} = \frac{1}{V_N\cdot p}\int_0^{p} V_N(p)\mathrm{d}p \tag{19}$$

Thus, in order to evaluate $\partial \ln p/\partial \ln N_t$, one has to obtain experimentally the function $V_N = V_N(p)$. This function is obtained directly in gas elution chromatography. Moreover, it can be obtained even from one elution peak.

We would like to emphasize here an additional advantage of the use of gas chromatographic data when calculating the function $(\partial \ln p/\partial \ln N_t)$. When the adsorption isotherm is known, given as usual in the form of a table (experimental points), then the graphical differentiation is needed in order to obtain the derivative $(\partial p/\partial N_t)$. Such a differentiation is rather laborious and also of small accuracy. On the other hand, the integration under the curve $V_N(p)$ may be performed very easily and accurately, as it may be performed automatically by means of electronic integrators.

Finally, chromatographic measurements may be very accurate, and are usually made many times more quickly than the classical measurement of adsorption isotherms.

EXPERIMENTAL

In order to illustrate the use of gas chromatographic data in the investigation of the adsorption mechanism on heterogeneous surfaces, we have measured the function $V_N(p)$ for four different adsorption systems, obtained by using two different solutes and two different adsorbents. One of the adsorbents used was a silica gel with large pores, produced by Polskie Oolczynniki Chemiczne (P.O.Ch) (Gliwice, Poland) while the other, with narrow pores, was prepared in the Academy of Mine and Metallurgy (Kraków, Poland). The support grains were carefully selected and the fractions 0.200–0.385 mm (wide-pore silica gel) and 0.150–0.200 mm (narrow-pore silica gel) were used in our measurements. The surface area measured by nitrogen was equal: 35.00 m^2/g for the wide-pore silica gel and 180 m^2/g for the narrow-pore gel.

We have also measured the surface area of the wide-pore silica gel using a mercury porosimeter and have found it to be 32.57 m^2/g. Pore distribution measurements have shown that the average pore radius of the narrow-pore silica gel is about 20 Å, whereas in the wide-pore silica gel it is about 140 Å. The bulk density measured by helium was equal to 2.1 g/cc for the wide-pore silica gel and 2.5 g/cc for the narrow-pore silica gel.

The solutes (cyclohexane and cyclohexene) used were produced by P.O.Ch. and further purified by us using a 5A molecular sieve. Hydrogen was used as carrier gas and was also purified by the 5A molecular sieve. The flow-rate was about 50 ml ($\pm 5\%$) per minute.

The chromatographic column of the wide-pore silica gel was 2.5 m × 4 mm I.D., and contained 21.06 g of adsorbent. The other one contained 5.40 g of the narrow-pore silica gel and was 1 m × 4 mm I.D.

The temperature was a little different for the chromatographic columns, 126.8° for the column containing the wide-pore silica gel and 126.3° ($\pm 0.1°$) for the other one.

The measurement conditions described above were chosen to eliminate dynamic effects as far as possible.

RESULTS AND DISCUSSION

In Fig. 1 is shown the method of extracting the information about adsorption mechanism from the function ($\partial \ln p/\partial \ln N_t$) and the adsorption isotherm, considered

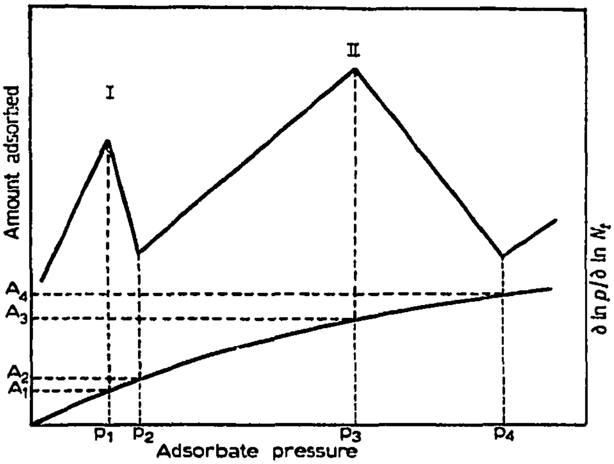

Fig. 1. A schematic diagram illustrating the method of extracting information about the adsorption mechanism from the function $\partial \ln p/\partial \ln N_t$ and the adsorption isotherm. The solid upper line denotes the idealized function ($\partial \ln p/\partial \ln N_t$) and the lower one the corresponding adsorption isotherm.

together. The solid line plotted below denotes the adsorption isotherm and the upper line the function ($\partial \ln p/\partial \ln N_t$) related to this isotherm (schematic picture).

According to our theory, the first linear part in the function $\partial \ln p/\partial \ln N_t$ concerns a primary characteristic adsorption on some area of the surface, which we shall denote as the I-st area of surface. This adsorption occurs until the pressure p_1 is reached, corresponding to a complete monolayer coverage of the I-st area of surface. The number of molecules adsorbed at pressure p_1 is simply equal to the number of adsorption sites within this area.

After the pressure p_1 is reached some specific multilayer adsorption begins on the I-st area of surface. The amount adsorbed secondarily on the I-st patch is equal to $(A_2 - A_1)$ moles per gram.

At pressure p_2 the next primary characteristic adsorption begins on some II-nd area of surface. This adsorption occurs to pressure p_3. The number of adsorption sites available for this adsorption (forming the II-nd area) is equal to $(A_3 - A_2)$ in moles per gram. The way of extracting further information is now obvious.

The solutes investigated by us are very similar chemical substances, except for the double bond in cyclohexene. We have chosen these substances in order to be able to draw more conclusions about the nature of the adsorption areas on the surfaces of our silica gels.

These areas seem to be simply different hydroxyl groups, for instance free, bound, geminal and reactive. From their nature it follows that they should exhibit different properties with respect to single and double chemical bonds. Therefore, by comparing the behaviour of cyclohexane and cyclohexene, one should extract more information about the nature of the silica gels investigated.

The experimental results for the four adsorption systems investigated are presented in Tables I–IV and in Figs. 2–5. Tables V and VI show the results of our

TABLE I

ADSORPTION OF CYCLOHEXANE ON WIDE-PORE SILICA GEL AT 126.8° —DEPENDENCE OF RETENTION VOLUME UPON ADSORBATE PRESSURE IN THE FREE GAS PHASE

V_N ($cm^3 \cdot g^{-1} \cdot 10^3$)	Pressure ($atm \cdot 10^3$)	V_N ($cm^3 \cdot g^{-1} \cdot 10^3$)	Pressure ($atm \cdot 10^3$)
2414.2	2.7772	1760.5	72.6812
2283.5	5.1905	1629.8	105.6609
2239.9	7.4680	1528.2	145.9075
2181.8	10.3528	1455.5	185.5972
2152.5	11.2214	1339.3	241.8950
2123.7	16.0475	1281.2	278.5696
2109.2	18.6579	1237.6	301.7222
2022.5	21.5000	1208.6	331.9352
1938.6	24.8939	1194.0	382.5622
1891.3	33.2857	1157.5	420.0000
1847.7	46.8343	1063.3	462.2764
1804.1	56.8950		

TABLE II

ADSORPTION OF CYCLOHEXENE ON WIDE-PORE SILICA GEL AT 126.8° —DEPENDENCE OF RETENTION VOLUME UPON ADSORBATE PRESSURE IN THE FREE GAS PHASE

V_N ($cm^3 \cdot g^{-1} \cdot 10^3$)	Pressure ($atm \cdot 10^3$)	V_N ($cm^3 \cdot g^{-1} \cdot 10^3$)	Pressure ($atm \cdot 10^3$)
9122.8	0.9102	5451.2	27.7564
8708.3	1.7241	5199.5	34.4095
8412.2	2.4003	4933.0	50.8378
7982.9	3.2853	4592.5	72.6488
7790.4	4.0927	4385.2	84.4942
7435.1	5.4417	4059.5	116.6622
7153.8	7.2493	3822.6	141.6311
6250.7	10.7609	3467.3	188.9267
6013.8	14.1875	3260.1	233.1853
5702.9	20.7575	3097.2	268.1761

TABLE III

ADSORPTION OF CYCLOHEXANE ON NARROW-PORE SILICA GEL AT 126.3° —DEPENDENCE OF RETENTION VOLUME UPON ADSORBATE PRESSURE IN THE FREE GAS PHASE

V_N ($cm^3 \cdot g^{-1} \cdot 10^3$)	Pressure ($atm \cdot 10^3$)	V_N ($cm^3 \cdot g^{-1} \cdot 10^3$)	Pressure ($atm \cdot 10^3$)
25451.0	1.8286	19075.0	35.0135
24470.0	3.7372	18242.6	44.6406
23560.0	5.9999	17479.3	53.7537
23036.0	7.2453	16334.3	76.2451
22516.0	8.7104	15380.1	98.1339
22450.0	10.1719	15082.7	122.9663
22310.0	11.3266	14513.7	140.8981
21854.0	14.5102	13515.8	169.6504
20871.0	18.2723	13216.7	205.2736
19983.0	25.0660		

calculations concerning the number of the available adsorption sites within the areas existing in the investigated adsorption systems.

It can be seen from Figs. 2–5 that for all these adsorption systems the upper investigated adsorbate concentrations yield retention volumes which are comparatively smaller than the retention volumes for the zero sample size of solute. Further, the changes in the function V_N *vs.* p are small. Of course, such concentrations correspond to comparatively small derivatives (and their changes) in the appropriate adsorption isotherms. In other words, in every case concentrations of adsorbate were reached corresponding to plateaus on the appropriate adsorption isotherms. Thus,

TABLE IV

ADSORPTION OF CYCLOHEXENE ON NARROW-PORE SILICA GEL AT 126.3° —DEPENDENCE OF RETENTION VOLUME UPON ADSORBATE PRESSURE IN THE FREE GAS PHASE

V_N ($cm^3 \cdot g^{-1} \cdot 10^3$)	Pressure ($atm \cdot 10^3$)	V_N ($cm^3 \cdot g^{-1} \cdot 10^3$)	Pressure ($atm \cdot 10^3$)
56220.0	0.9118	41973.2	12.9384
54270.0	1.8291	40142.0	18.3195
51870.0	2.7732	38482.8	23.4195
50542.0	3.3972	37008.0	29.3625
49402.0	4.2776	34795.8	41.1331
47570.0	5.9281	32583.6	55.2658
46441.0	7.4453	31477.4	69.5227
45100.0	8.5999	30371.3	82.4406
43611.5	9.6398	29849.0	95.2750

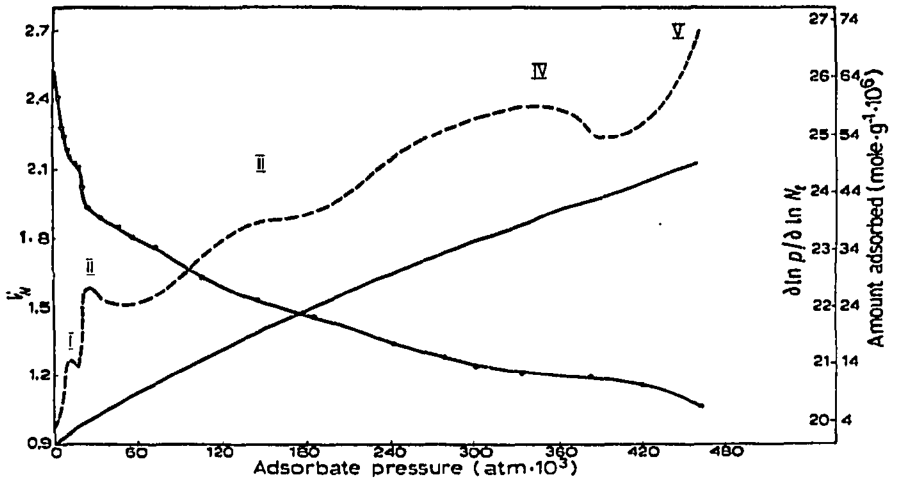

Fig. 2. Adsorption of cyclohexane on wide-pore silica gel. The solid line with circles is the experimental curve $V_N = V_N(p)$. The dashed line denotes the calculated function ($\partial \ln p / \partial \ln N_t$) and the solid one the corresponding adsorption isotherm. V_N in $cm^3 \cdot g^{-1}$.

according to Hobson's theory, the concentrations investigated by us should detect all kinds of adsorption areas existing on the silica gel surfaces investigated.

The first general and obvious conclusion which can be drawn from the figures is that there exist five types (areas) of adsorption site for both cyclohexane and cyclohexene on the two silica gel surfaces investigated. This follows from the fact that one may distinguish five approximately linear parts in the plots ($\partial \ln p / \partial \ln N_t$) (having positive slopes) for all the investigated adsorption systems. Such a conclusion is in excellent agreement with the investigations of Kiselev and Łygina[16,17], Snyder and Ward[18] and Peri and Hensley[19]. From their results, in addition to the

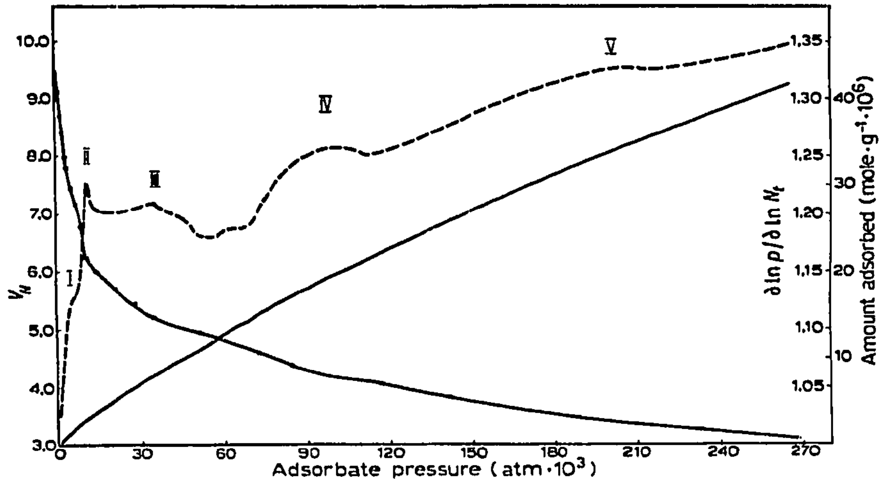

Fig. 3. Adsorption of cyclohexene on wide-pore silica gel. The solid line with circles is the experimental curve $V_N = V_N(p)$. The dashed line is the calculated function ($\partial \ln p/\partial \ln N_t$) and the solid one the corresponding adsorption isotherm. V_N in $cm^3 \cdot g^{-1}$.

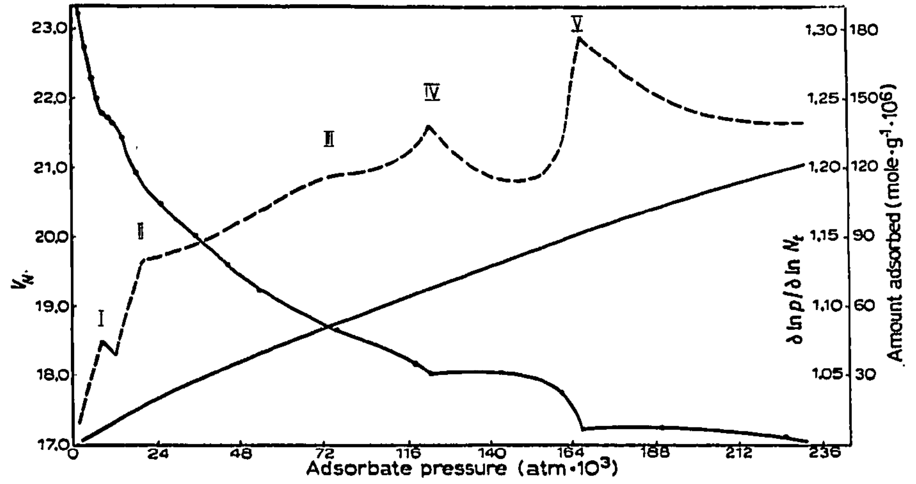

Fig. 4. Adsorption of cyclohexane on narrow-pore silica gel. The solid line with circles is the experimental curve $V_N = V_N(p)$. The dashed line is the calculated function ($\partial \ln p/\partial \ln N_t$) and the solid one the corresponding adsorption isotherm. V_N in $cm^3 \cdot g^{-1}$.

free, bound, reactive and geminal hydroxyls, there are also siloxane groups as adsorption sites.

Even at first sight, one may detect a great similarity between the functions ($\partial \ln p/\partial \ln N_t$) for all the investigated adsorption systems. This probably demonstrates that the sequence of strength of adsorption sites is the same for all the adsorption systems.

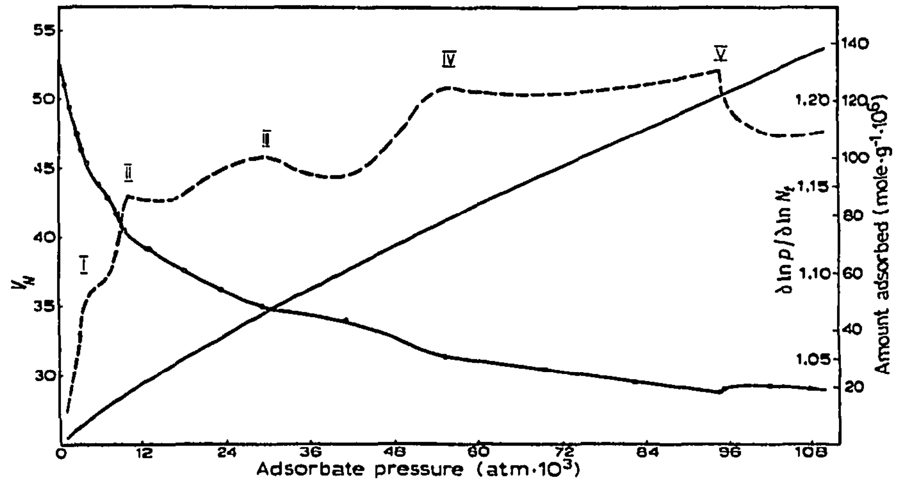

Fig. 5 Adsorption of cyclohexene on narrow-pore silica gel. The solid line with circles is the experimental curve $V_N = V_N(p)$. The dashed line is the calculated function $(\partial \ln p/\partial \ln N_t)$ and the solid one the corresponding adsorption isotherm. V_N in cm^3·g^{-1}.

As in the schematic Fig. 1, we shall denote the adsorption areas by the Roman numbers I, II, III, IV and V. There remains to be established in detail the sequence of strength in every adsorption system.

For this purpose consider the data presented in Tables V and VI. It has been found by a great number of investigators that the most reactive hydroxyls lie in rather narrow pores and therefore their contribution should increase as porosity increases. Consequently, the contribution of the most active sites of the I-st and of the II-nd type (adsorption at lowest adsorbate pressures) should be much greater for narrow-pore than for wide-pore silica gel.

TABLE V

ADSORPTION OF CYCLOHEXANE AND CYCLOHEXENE ON WIDE-PORE SILICA GEL

The capacities of the appropiate adsorption areas and their percentage contributions estimated from the function $(\partial \ln p/\partial \ln N_t)$ are given.

Type of surface area	*Cyclohexane*		*Cyclohexene*	
	Amount adsorbed per gram (mole·10^6)	*Percentage contribution of sites*	*Amount adsorbed per gram (mole·10^6)*	*Percentage contribution of sites*
I	1.1	6.15	2.0	13.50
II	0.6	3.41	1.2	8.10
III	6.7	38.10	3.3	22.50
IV	9.2	45.00	8.3	29.39
V	2.7	13.00	13.3	55.90

TABLE VI

ADSORPTION OF CYCLOHEXANE AND CYCLOHEXENE ON NARROW-PORE SILICA GEL

The capacities of adsorption areas and their percentage contributions estimated from the function ($\partial \ln p/\partial \ln N_t$) are given.

Type of surface area	*Cyclohexane*		*Cyclohexene*	
	Amount adsorbed per gram (mole· 10^6)	*Percentage contribution of sites*	*Amount adsorbed per gram (mole· 10^6)*	*Percentage contribution of sites*
I	6.7	8.94	1.2	1.57
II	7.0	9.27	6.0	6.64
III	38.2	50.65	21.2	23.46
IV	13.0	17.21	20.8	23.02
V	10.5	13.90	41.2	45.59

In fact this is observed in Tables V and VI for cyclohexane as shown by the percentage contributions. The opposite occurs for cyclohexene. Such a different behaviour can be explained on the basis of steric effects, using the concept of an oriented adsorption of cyclohexene molecules.

As has been detected, the most active centres of the I-st and of the II-nd type lie in narrow pores. Thus, steric effects should in general decrease the number of available adsorption sites in the narrow pores. This opposite effect should be especially strong in the case of cyclohexene, for the reason described below. Because of the double bond in cyclohexene, some adsorption positions on silica gel surfaces are preferred by cyclohexene molecules. In our opinion, these are the positions in which cyclohexene molecules stand on adsorbent surface, attached by the double bond. Of course, such "standing" positions in pores will hinder the penetrations of the pores by other cyclohexene molecules. The greater the porosity (smaller pores), the stronger should be the hindering of penetrations. In the case of cyclohexene molecules, this effect becomes predominant, and the percentage contribution of the I-st and II-nd types of adsorption site becomes greater in the case of the wide-pore silica gel. The same effect of the "standing" positions should lead to an effective increase in the available adsorption sites when the adsorption sites lie on wide-plane surfaces (free and geminal hydroxyls). This arises from the fact that such "standing" positions should give better packing of molecules on wide-plane surfaces. Moreover, one may assume that this better packing should be greatest in the case of geminal hydroxyls, where the hydroxyl groups are very near to one another.

Let us consider the ratios of appropiate adsorption sites available for cyclohexane and cyclohexene in the case of wide-pore silica gel, where this effect should appear in a more clear form (larger pores, have more wide-plane surfaces). They are equal to $2.0/1.1 = 1.82$ for the I-st type, $1.2/0.6 = 2.0$ for the second type and $3.3/6.7 = 0.49$ for the III-rd type, as shown in Table VI. From this comparison it follows that the greatest increase in the ratio is in the second type of site, *i.e.* geminal hydroxyls. Assuming that the reactive hydroxyls are the strongest adsorption sites, we get the following sequence of strength: reactive>geminal>free>bound>siloxane (the sequence proposed in general by Snyder[20] was reactive>free>bound).

From Figs. 2–5, one can draw other interesting conclusions, which are in agreement with those developed above. Namely, one may assume that because of the standing positions of the cyclohexene molecules, the formation of a multilayer of cyclohexene in the pores will be hindered. Really, for the silica gels, the formation of the multilayer on the I-st area of surface is observed only in the case of cyclohexane. According to our knowledge the I-st area of surface consists of reactive hydroxyls in very narrow pores.

Now consider the formation of a multilayer on the II-nd area of surface (geminal hydroxyls). They lie in pores too, though probably in wider ones. This follows from the fact that the formation of a multilayer on the II-nd area is observed for both cyclohexane and cyclohexene, in spite of the standing positions of cyclohexene molecules. However, it may be also observed that the formation of a multilayer is still greater in the case of cyclohexane, which means that the standing positions still hinder in some measure the formation of the cyclohexene multilayer.

A very interesting problem seems to be the formation of a multilayer on the III-rd and IV-th areas of surface.

Let us first consider the secondary (multilayer) adsorption on the III-rd area of surface (free hydroxyls). It is seen from our figures that for both the investigated silica gels, the formation of the cyclohexene multilayer is much stronger than that of cyclohexane. According to our knowledge[20], a great part of the free hydroxyls lies in narrow pores. Therefore explanations using the concept of steric effects are not possible in this case.

A possible explanation may be based on the theory of third-order interactions in physical adsorption. Following the calculations of Sinanoglu and Pitzer[21] and Yaris[22] and McLachlan[23], the presence of the surface has the effect of increasing the adsorption energy for the molecules adsorbed in the second layer (perturbation of the molecule–molecule interactions due to the presence of solid). This additional intermolecular attraction is about 10–15% attraction depth for two adsorbate molecules in the bulk phase. The greater the adsorption energy in the first layer, the greater is the additional attraction energy in the second layer. As cyclohexene is adsorbed much more strongly than cyclohexane, the additional attraction, and hence the multilayer adsorption on the II-rd area of surface, is much stronger in the case of cyclohexene.

Just the opposite effect is observed for the IV-th and V-th areas of surface, where the formation of a cyclohexane multilayer is much stronger. The following explanation may apply. The secondary adsorption is affected by two types of interaction, *viz.* (a) short-range interactions between the primarily and secondarily adsorbed molecules and (b) long-range attractive forces between the surface and the secondarily adsorbed molecules. Of course, the long-range attraction decreases as the distance from the surface increases. Therefore, the standing positions of the primarily adsorbed cyclohexene molecules have the effect of increasing the distance from the surface, where the second and higher layers may be formed, and through it the effect of decreasing the adsorption energy for the secondary adsorbed cyclohexene molecules.

Of course, the effect described above exists for every area of surface, although up to the III-rd patch the third-order effects play a predominant role because of the strong adsorptive energy of the I-st, II-nd and III-rd types of adsorption sites. In the case of the IVth and V-th area of surface, however, the adsorption energy in the first layer, and hence the additional third-order energy in second layer, are comparatively small and the standing effects become predominant. From their nature relative to the long-range gas–solid attraction, it follows that they should lead to increased multilayer adsorption of cyclohexane in comparison with cyclohexene, which is in fact observed.

There remains to be discussed the possible influence of dynamic effects in gas–solid chromatography on the obtained adsorption data.

This problem was investigated by a number of authors, but the work of Huber and Keulemans[24], Belyakova *et al.*[25], Dallimore *et al.*[26] and Zhukhovitskii and Turkeltaub[27] is here of basic importance. The most recent and complete theoretical considerations may be found in the papers of Huber and Gerritse[28] and Wicke[29] and Haul[4]. These authors discuss the role of column length, carrier gas velocity and kind of carrier gas used in the measurements, and also the role of the ratio of grain diameter to average pore radius and to column diameter.

In conclusion, one may say of the work of there authors that a suitable choice of these parameters decreases the dynamic effects to a degree of no practical importance. This conclusion is illustrated by many experimental data in the monograph by Kiselev and Jashin[30].

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