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DISCUSSION OF ADSORPTIVE PROPERTIES OF COLUMN PACKINGS IN GAS CHROMATOGRAPHY

I. ENERGY PROPERTIES OF THE MATERIAL SUPPORTING LIQUID STATIONARY PHASES

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SUMMARY

The method for the determination of the distribution of the adsorption potential, G, was used for the estimation of the adsorption properties of chromatographic supports and adsorbents. It is suggested that the energy heterogeneity of adsorbent and support surfaces can be estimated qualitatively by the determination of the maximum ($G_{max.}$) and minimum ($G_{min.}$) values of the potential; this characteristic can also be used for the classification of supports and adsorbents. Further suggestions are made concerning the presumption that for strong energy heterogeneity of adsorbent and support surfaces, steps can appear on the adsorption isotherms due to the co-existence of surface sites which have very different values of G.

The Polish diatomite support, Diatomite D2, was investigated using several test solutes of different chemical character. The interactions of the test solutes with the surface of the support are dicussed, relating these interactions with the corresponding values of $G_{max.}$ and $G_{min.}$.

INTRODUCTION

There is considerable experimental evidence that the surfaces of solids are energetically non-homogeneous and that there exist separate specific active adsorption sites on these surfaces. This is caused by the non-uniform distribution of the free surface energy due to roughness of the surface and the existence of cracks, dislocations, network defects, etc. The adsorption equilibrium (adsorption isotherm), the kinetics of adsorption, variation of heats of adsorption and activation energies are closely related with the energetic non-homogeneity of the adsorbent surface.

The adsorbents and supports employed in gas chromatography (GC) usually belong to such non-homogeneous materials. In chromatographic processes, the non-homogeneity is reflected by peak asymmetry and by the variation of retention times with the sample size, which may be caused by non-linearity of the adsorption isotherm.

The system adsorbent–adsorbate is characterized by the heat of adsorption or the adsorption isotherm. Because of the non-homogeneity of the adsorbent surface,

the results obtained are evidently incomplete since only a statistical description is given of the surface properties. Similarly, the shape of the adsorption isotherm gives only qualitative information on the adsorption process.

According to POLANYI's theory of adsorption[9,12], the system adsorbent–adsorbate can be characterized by the adsorption potential which is equal to the energy of interaction between the molecules of the adsorbate and the adsorbent surface. In view of the non-uniform distribution of the free surface energy, the values of the adsorption potential are different at different points on the surface and at different distances from the surface.

In an earlier paper[1], we described a chromatographic method for the determination of the distribution of the adsorption potential on adsorbent surfaces. We shall apply this method to the investigation of column packings in adsorption chromatography. The interest in this problem is due to the fact that in numerous problems in chromatography, the non-homogeneity of the adsorbent surface is usually neglected, mainly because of the difficulties in its estimation. Such approximation is justified if the variations of the adsorption potential are not significant, and thus do not affect the separation of the chromatographed solute and the peak shape.

However, there are no reports in the literature on the distribution of adsorption potentials on the support materials for column packings.

Nevertheless, some conclusions concerning these properties can be drawn from chromatographic data. The results of numerous investigations[2-4] suggest that the properties of the stationary phase may depend on the adsorption properties of the support material. Therefore, it is interesting to investigate systems composed of the solute and of support material covered with the stationary phase in an amount that is insufficient for the contribution of bulk absorption to be large in comparison with adsorption during the passage of the solute through the column.

In the present paper, we shall deal with the differences of the adsorption potentials for a typical chromatographic support and for solutes of various chemical character, as well as with the nature of the adsorption sites which cause these differences.

EXPERIMENTAL

The Polish support material Diatomite D2 (ref. 5,6) was employed in the investigations, using a gas chromatograph produced by W. Gide 18.3 (G.D.R.) with a thermal conductivity detector. The test solutes were n-pentane, n-heptane, furan, chloroform and carbon tetrachloride. 1–5 μl samples were introduced using Hamilton microsyringes. From the retention times of test solutes for various sample sizes and at given temperatures, the absolute retention volumes, V_N, were calculated and then extrapolated to zero sample size (V_{NE}).

The temperatures at which measurements were made and the corresponding extrapolated retention volumes are given in Table I. From these data, graphs of $\log V_N/T$ vs. $1/T$ were plotted and $G_{max.}$ and $G_{min.}$, proportional to $\dfrac{\mathrm{d} \ln V_N/T}{\mathrm{d}\, 1/T}$ were determined from the plots[1,13,14*].

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* It is assumed, according to the literature[1], that the term $\dfrac{\mathrm{d} \ln V_N/T}{\mathrm{d}\, 1/T}$ is proportional to the adsorption enthalpy (heat of adsorption) equal, in good approximation, to the value of adsorption potential.

TABLE I

RETENTION VOLUME DATA EXTRAPOLATED TO ZERO SAMPLE SIZE AT VARIOUS TEMPERATURES

Pentane		Heptane		Furan		Chloroform		Carbon tetrachloride	
$T(°K)$	V_{NE}	$T(°K)$	V_{NE}	$T(°K)$	V_{NE}	$T(°K)$	V_{NE}	$T(°K)$	V_{NE}
360.25	13.03	361.2	61.04	329.3	312.68	347.3	65.8	359.6	28.82
371.8	9.2	370.1	42.5	335.8	220.72	359.6	42.64	368.8	22.36
376.8	7.92	376.0	34.56	347.3	128.18	368.8	30.17	383.6	14.94
383.2	7.06	383.4	28.15	359.6	83.97	376.0	22.55	410.2	7.28
404.3	4.43	396.5	19.15						
408.0	4.07	410.2	13.61						

The other experimental conditions were as follows: gas flow rate was constant and equal to 10 ml/min at the temperature of column operation; the carrier gas was purified on a pre-column packed with Molecular Sieve 5A; a steel column 3 m long and 4 mm I.D. was used; the support material was activated before chromatographic experiments in a stream of carrier gas for 3 h at 250°.

RESULTS AND DISCUSSION

Fig. 1a represents log V_{NE}/T vs. $1/T$ plots for n-pentane, n-heptane, carbon tetrachloride and chloroform, and Fig. 1b the analogous relationship for furan. The
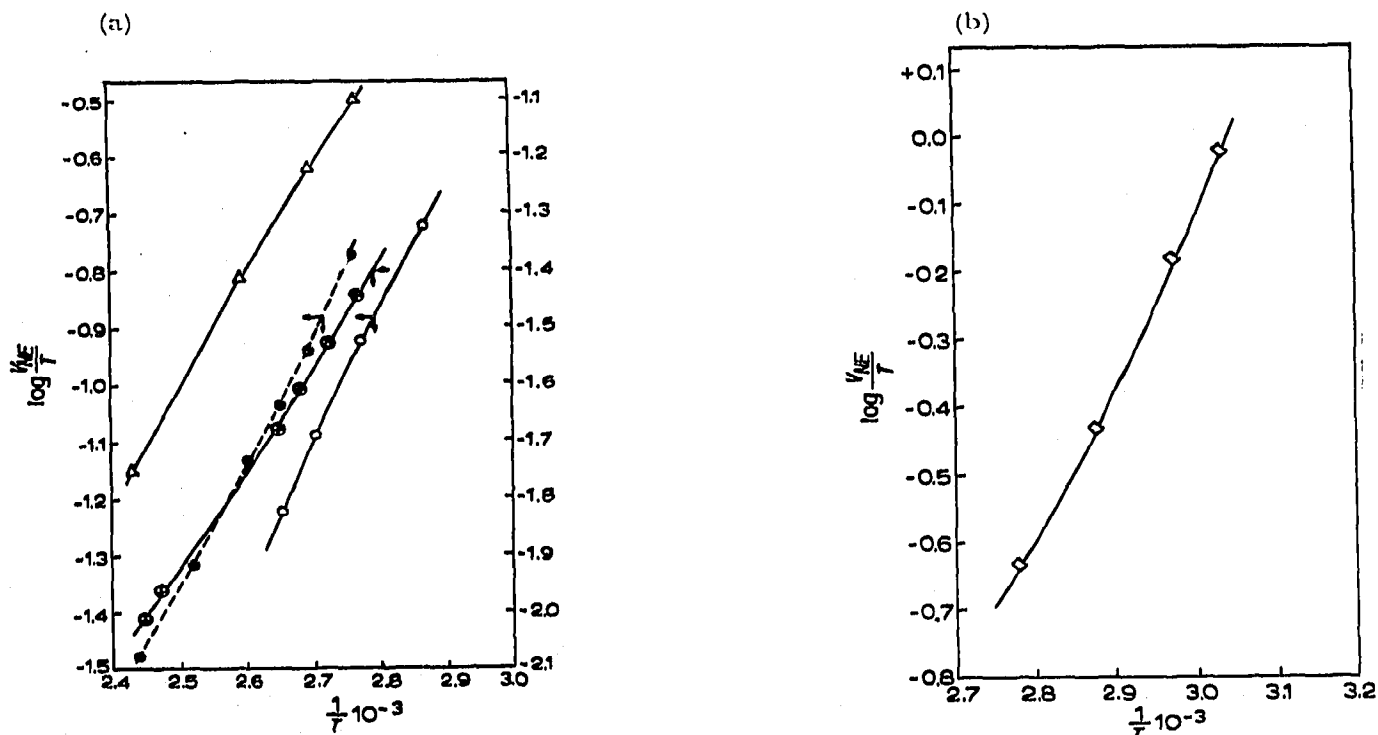

Fig. 1. Logarithm of fully corrected retention volume divided by temperature for four solutes on Diatomite D2 (extrapolated to zero sample size) as a function of the reciprocal of the absolute temperature of the measurements. (a) ○, chloroform; ●, heptane; ⊕, pentane; △, carbon tetrachloride and (b) ◇, furan.

values of log V_{NE}/T shown on the right-hand ordinate refer to carbon tetrachloride and n-pentane. It is evident that the relationships are non-linear in all cases, which seems to indicate that the surface of the material investigated is energetically non-homogeneous.

It is characteristic that the curves for n-heptane, n-pentane and furan are concave to the ordinate axis, whereas those for carbon tetrachloride and chloroform are convex. This is presumably due to different molecular interactions between the adsorbate molecules and the surface of the support material which occur in the adsorption process. In the first case, it can be assumed that the hydrocarbons (n-pentane and n-heptane) interact with the diatomite non-specifically, whereas the interactions of the chlorinated hydrocarbons are specific in character.

In Table II the values of $G_{min.}$, $G_{max.}$ and $\Delta G = G_{max.} - G_{min.}$ are given for the five solutes investigated.

TABLE II

MINIMUM ($G_{min.}$) AND MAXIMUM ($G_{max.}$) ADSORPTION POTENTIALS

G (cal/mole)	Pentane	Heptane	Furan	Chloroform	Carbon tetrachloride
$G_{min.}$	7400	8800	8000	9500	8200
$G_{max.}$	9100	11000	13000	11600	11900
ΔG	1700	2600	5000	2100	3700

In the case of chloroform, it can be assumed that there are two main types of active sites on the support surface, due to the presence of silanol and siloxane groups. The molecules of chloroform can interact with these sites by formation of hydrogen bonds:

$$-\overset{|}{\underset{|}{Si}}-O-H \cdots\cdots ClCHCl_2 \text{ or } {>}O \cdots\cdots HCCl_3$$

The value of $\Delta G = 2.1$ kcal/mole observed for chloroform can be ascribed to the difference between the energy of interactions of the first and second types. It can be seen that the differences between $G_{max.}$ and $G_{min.}$ for carbon tetrachloride and furan are greater than for chloroform, which has a permanent dipole moment. It is generally assumed that the dipole moment of carbon tetrachloride in the ground state is zero. In reality, at room temperature a large proportion of carbon tetrachloride molecules are in an excited vibrational state, ca. 13% of the total number of molecules possessing a definite permanent dipole moment of $\mu = 0.9\ D$ (ref. 7). In other words, the solvent can be considered as a solution of excited polar molecules in a liquid composed of non-polar molecules in the ground state. The investigations have shown that the molecules are relatively long-lived, ca. 10^{+10} sec, the time of reorientation being 10^{-11}–10^{-12} sec, i.e. lower by at least one order of magnitude. It can be assumed that under the effect of an external field (in this case, the effect of the adsorbent) a "dynamic polarization" of the molecules takes place. A comparison of the total polarizabilities of chloroform and carbon tetrachloride is in favour of the latter solvent; thus, $\alpha_{CHCl_3} = 8.23\ \text{Å}^3$ and $\alpha_{CCl_4} = 10.5\ \text{Å}^3$. Since the polarizability determines the energy

of non-specific dispersion interaction, this largely explains the larger values of G for carbon tetrachloride.

It is interesting to compare the average time of adsorption of a molecule of carbon tetrachloride with its lifetime, τ_t, in the excited state. The relationship between the adsorption time, τ, or the average time which the molecule spends on the adsorbent surface, and the energy of adsorption, G, is given by the equation

$$\tau = \tau_0 \exp G/RT$$

where $\tau_0 \approx 10^{-13}$ sec. ADAMSON[8] maintains that for $G = 9$ kcal/mole, $\tau = 4 \times 10^{-7}$ sec. For larger values of G, the time τ is correspondingly longer. Therefore, for carbon tetrachloride, $\tau > \tau_t$; this seems to indicate that the interactions between carbon tetrachloride molecules and the adsorbent surface may be partly specific in character and that stable complexes between hydroxyl groups of the support and carbon tetrachloride molecules may be formed.

In the case of furan, the larger value of ΔG may be explained by its aromatic character. The interactions of the solute with the adsorbent surface are more complex than those of the remaining solutes. It can form hydrogen bonds both with the π electrons of the ring as well as with the free electron pairs of the oxygen atom, as shown
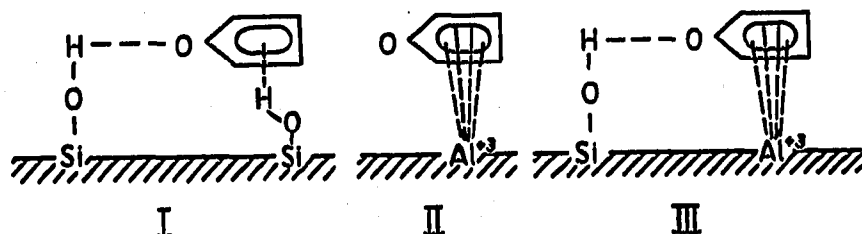

Fig. 2. Schemes illustrating the interaction of the furan molecule with the adsorbent surface.

in scheme I in Fig. 2, and since the support contains, besides SiO_2, some oxides of mono-, di- and trivalent metals (Na_2O, CaO, Al_2O_3, Fe_2O_3, etc.), then electrostatic interactions of the types shown in schemes II and III are also possible.

In these cases, the role of the electronegative groups is played, as before (scheme I), by the electrons of the aromatic ring, under the influence of the positive electric field of the cation. The force of this field, and thus also the energy of adsorption, is determined by the type of cation. The formation of a single hydrogen bond between a surface hydroxyl group and the oxygen atom of the furan molecule is also possible, which in the case discussed is more probable than the formation of two hydrogen bonds (scheme I). It is obvious that the contributions of the various types of interactions between furan molecules and the support surface is determined by steric factors.

Such modes of interactions between furan molecules and the support surface must entail high retention times and retention volumes. In fact, it follows from Table I that furan, in spite of its having the lowest boiling point of the solutes investigated, has the highest values of retention volumes.

It can be seen that also in the case of carbon tetrachloride and chloroform, the energy of adsorption depends largely on the force of the electric field due to cations on the support surface. The solute molecules in the electric field are polarized. Such orientation polarization can also be presumed in the case of furan.

It is known that ionic structures ($\mu = 0.71\ D$) participate in the mesomerism and it is not impossible that under the effect of the electric field of the cation (scheme II) the electronic system of the furan molecule is polarized, thereby becoming similar to one of the limiting structures. The polarized molecule of furan is not identical with the limiting structure of the isolated molecule, but is in a transition state in which the interaction with the adsorbent surface takes place.

CONCLUSIONS

The energetic heterogeneity of the surface of solid powdered materials depends mainly on the geometrical heterogeneity, including the defects of the crystal network and its surface defects, porosity (including the size and tortuosity of the pores), mechanical defects of the surface, etc., and the chemical heterogeneity, *i.e.* the presence on the surface, in addition to the main components of the material, of various impurities, mainly ions and atoms of metals.

The range of the heterogeneity (from $G_{min.}$ to $G_{max.}$) is closely related to the type of solute used as the absorbate. This is understandable from the viewpoint of correlation between the size of the solute molecule, its structure and the size of the pores of the adsorbent and the surface area occupied by one solute molecule in the adsorption process.

Energetic heterogeneity of surfaces of chromatographic supports and adsorbents in relation to a given adsorbate can be qualitatively estimated by the determination of $G_{max.}$ and $G_{min.}$. This follows from the experimental fact that even a negligible admixture of sites of high potential can cause marked anomalies in the sorption process (diffuseness and asymmetry of peaks of chromatographed solutes, variation of the retention parameters with the sample size, occurrence of irreversible adsorption).

All methods of deactivation of supports and adsorbents depend on the removal or blocking of the most active surface sites whose interactions cause the formation of specific strong bonds or groupings. For instance, the detection on the support surface of a high adsorption potential suggests *a priori* that the material requires deactivation before use, irrespective of the quantitative contribution of the most active sites.

From the above-mentioned nature of the adsorptive sites, which cause the energetic heterogeneity of the surface of powdered materials, the following commonly used methods of pre-treatment of the support can be deduced: (1) removal of ions and atoms of heavy metals by treatment with acids and alkalis; (2) heating of the powdered material, also with soda or mixtures of soda and alkali chlorides; (3) blocking of active sites (hydroxyl groups) by chemical reactions, usually with silanes or alcohols; and (4) blocking of active sites by treating the support with small amounts of a strongly adsorbed substance, or by addition of the substance to the stationary phase.

It should be pointed out that the simple application of one of these methods frequently leads to side effects (for instance, in the first and second cases, the total porosity and the active surface area are increased). However, it always causes the difference between $G_{max.}$ and $G_{min.}$ to be decreased, so that the energetic homogeneity of the surface is increased. An ideal support material should have a smooth surface without pores and crevices. In practice, such a support is difficult to obtain, as well as

being of little use in view of its low capacity to retain the stationary liquid phase. Therefore, a more useful material, although difficult to prepare, would be a support possessing a constant amount of active sites (of as similar adsorption potential as possible) per unit surface area, $d\Delta G/dS$ = constant. The achievement of this entails the decrease of the active surface of the support to values of the order of 0.1 m^2/g (Chromosorb G, Gas-Chrom Q); a sufficient capacity to retain the stationary phase is secured by the formation of a macroporous structure during the preparation process (with spherical particles of the support being conglomerates of numerous fine particles).

From the data reported in the present paper and in previous publications[5,6,9] on the properties of Polish Diatomite D (crude preparation), the place of this support among the commonly used chromatographic support materials can be found[10]. In particular, taking into account the presence of large amounts of iron oxides in this material, and its narrow pores[5], it can be considered as a support material of moderately good working properties[10], like sterchamol, Chromosorb P and Firebrick C-22. It should be pointed out that in the investigations of BLANDENET AND ROBIN[10], the method for the determination of pore volume distribution using a mercury porosimeter cannot detect the presence and determine the contribution of narrow pores of the order 20–40 Å found for Diatomite D from the B.E.T. isotherm[5]. It seems likely that pores in this range are also present in the above-mentioned supports similar to Diatomite D, which determines their relatively high adsorption activity and catalytic properties, as well as the marked energetic heterogeneity of their surfaces.

It can be presumed that the energetic heterogeneity of adsorbents and supports for GC influences the shape of the adsorption isotherm (particularly in the range of low equilibrium concentrations), causing even the appearance of bends and inflections (so-called steps and waves) due to the co-existence of sites with very large differences in values of G on the surface.

Further investigations of these phenomena are now in progress and the results will be published in future papers.

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