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ADSORPTION PROPERTIES OF SILANIZED AND CARBOWAX-MODIFIED SUPPORTS FOR GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

Two of the best supports for gas-liquid chromatography were studied for adsorption activity using adsorbates with different polarities and molecular structures. The thermodynamics of adsorption were determined on the best commercial silanized support (Chromaton N Super) and on Carbowax-modified Chromaton N AW. The experimental data indicate the presence of some specific adsorption sites on the silanized support surface while free hydroxyls are eliminated from this surface. Metal cations seem to be the active sites. When using the modified support the adsorption isotherms are linear, while non-linearity of the adsorption isotherms for oxygen-containing adsorbates is observed on the silanized support.

INTRODUCTION

Creation of the ideal support is one of the most urgent problems in gas-liquid chromatography (GLC). The general properties of many supports have been reviewed^{1,2}, particular attention being paid to commercial supports. At present, silanized supports such as Chromosorb W HP, Chromosorb 750 and Chromaton N Super seem to be the best for GLC. However, even these supports have some disadvantages for polar solutes on non-polar or weakly polar stationary phases (peaks asymmetry, tailing, etc.). Even after taking into account the non-linearity of the sorption isotherm for these solutes, the "self-modification" effect³ remains which prevents the determination of reproducible data for mixtures of polar solutes.

Carbowax modified according to the Aue procedure^{4,5} has almost ideal properties for GLC with non-polar stationary phases⁵. The "self-modification" effect is not observed on the modified support.

Many papers have reported "bad" and "good" support properties, mainly when qualitative parameters for the supports were compared (for example, peak symmetry, tailing, possibility of elution). No thermodynamic adsorption parameters for the best silanized supports and the Carbowax modified support have been reported, thus preventing discussion of the support surface. This paper describes a comparative thermodynamic study of adsorption on the two best support surfaces: silanized and modified.

EXPERIMENTAL

Instruments and calculations

The experiment was performed on a Chrom-42 (Laboratorní Přístroje) instrument with a flame-ionization detector. Stainless-steel tubes (2.4 m × 3 mm I.D.) were used as columns and packed with the support and conditioned at 260°C overnight.

Chromaton N AW (Lachema, Czechoslovakia) was chosen as the basic material for the compared supports; Chromaton N Super (Lachema) was the best silanized support. The same basic material (Chromaton N AW) was used for the Carbowax modification; therefore, the compared supports have the same bulk properties. The modification procedure was similar to that described by Aue and co-workers^{4,5}: Chromaton N AW was coated with 0.2% polyethylene glycol 15000, and then conditioned at 260°C for 6 h in a helium stream. The extraction step was omitted.

The relative retentions, r , of some solutes were measured using benzene as the standard. The relationship between $\ln r$ and $1/T_c$ (T_c = column temperature in °K) was plotted and the r value at 50°C was calculated from this graph. The same relationship was used to calculate the relative molar heats of adsorption, ΔH_a^0 , as described elsewhere.

The entropic selectivity, F^0 , was calculated as⁶

$$F^0 = R \ln r + 0.535 \Delta H_a^0/T \quad (1)$$

where R is the gas constant.

The relative mean standard deviation for r was about 0.1% for the cases with linear isotherms and up to 1% for those with non-linear isotherms; for ΔH_a^0 the corresponding deviations were 3 and 8%, respectively.

When the adsorption isotherm is non-linear, the net retention volume, V_N , depends on the sample amount or peak height, h . The following equation was used to take account of the non-linearity of the adsorption isotherm⁷, where A and B are constants:

$$V_N = B + A/\log h \quad (2)$$

The relationship between V_N and $1/\log h$ was plotted using 3–5 experimental points, and the V_N value for a chosen peak height thus calculated.

The recorder full scale was 10^{-11} A (chart width 250 mm); peak height was measured in mm. The chosen peak height for the calculations (isobaric retention) was the value at which $1/\log h = 0.3$. Isobaric thermodynamic functions of adsorption were calculated by using the isobaric retention data as elsewhere⁷.

The degree of non-linearity of the adsorption isotherm was calculated by using the following equation⁷:

$$A^* = (V_{N_{0.4}} - V_{N_{0.3}})/V_{N_{0.3}} \quad (3)$$

The subscripts 0.3 and 0.4 relate to the corresponding values of $1/\log h$. The A^* value is expressed in relative units and this parameter is valuable for comparison of adsorbents at chosen vapour pressures of the adsorbate.

TABLE I

ADSORPTION CHARACTERISTICS OF THE ADSORBATES ON THE SILANIZED (S) AND CARBOWAX-MODIFIED (M) SUPPORTS

 ΔH_a^0 in kcal/mole, F^0 in cal./°K · mole. The standard temperature was 50°C.

Adsorbate	S			M		
	<i>r</i>	ΔH_a^0	F^0	<i>r</i>	ΔH_a^0	F^0
Carbon tetrachloride	0.735	7.2	11.98	0.902	-9.5	-16.8
Chloroform	0.564	-4.6	-9.17	1.78	2.1	4.8
1,2-Dichloroethane	1.331	-14.8	-25.3	2.05	4.5	9.3
Ethyl acetate	9.04	6.5	15.7	0.925	-3.7	-6.6
Methyl ethyl ketone	10.1	6.6	16.1	1.01	-2.9	-5.0
<i>n</i> -Propanol	17.1	16.6	17.1	2.97	2.5	6.5

Because of the low adsorption activity of the compared supports the flow-rate of the carrier gas was chosen to be sufficiently low (about 5–7 ml/min) that the retention times could be determined with high precision. These determinations were performed isothermally in the column temperature range 40–70°C.

The adsorbates studied are listed in Table I.

RESULTS AND DISCUSSION

The experimentally determined support properties (S = silanized support, M = the modified one) are listed in Table I. First we discuss the relative molar heats of adsorption which are related to the energy of intermolecular forces at the support surface.

Carbon tetrachloride is a non-polar adsorbate with zero dipole moment. Its ΔH_a^0 on the silanized support is 7.2 kcal/mole which indicates a very low energy of intermolecular forces as compared with benzene. The benzene molecule also has a dipole moment of zero, however it has a π -electron cloud that may interact to form complexes with metal cations which are on the surface of the silanized support. The cations are formed by calcination of white supports, and some metal cations were absorbed by diatomites from sea water (Fe, Al, etc.)⁸⁻¹⁰. Upon acid treatment of the white support some metal cations are eluted from the surface. However, sodium having a high diffusion coefficient reaches the surface even after acid washing. A small amount of heavy metal cations also remains on the support surface after acid washing. All these cations may form π -complexes with benzene molecules, thus leading to strong interactions between benzene and the support surface. Additional evidence for this is the relative molar heat of adsorption for carbon tetrachloride on the modified support: this value of -9.5 kcal/mole means that benzene is less strongly bonded with the support surface than is carbon tetrachloride. Indeed, the modified surface is coated by a uniform film of the modifier, therefore no specific adsorption centres are present on the surface. A marked difference in the nature of the compared support surfaces is illustrated by the relative retention data for the supports.

The 1,2-dichloroethane molecule has two microdipoles between the atoms of

carbon and chlorine. The orientation forces with the support surface may be revealed for this molecule unlike the non-polar molecules benzene and carbon tetrachloride. When using the silanized support the relative molar heat of adsorption of dichloroethane is 22 kcal/mole less than for carbon tetrachloride although the molar refractions for the two molecules are about the same. This shows the strong adsorbate-absorbent interaction with orientation forces. When using the modified support, the molar heat of adsorption for dichloroethane is 14 kcal/mole more positive than that for carbon tetrachloride, clearly indicating the different natures of the compared supports.

Chloroform may form weak hydrogen bonds, however, the dipole moment of this molecule is low because of shielding C-Cl bonds. On the compared supports the molar heat of adsorption for chloroform is intermediate between those for carbon tetrachloride and dichloroethane, indicating the same change of the intermolecular interaction throughout the series of chlorinated hydrocarbons. In addition, the energy of the hydrogen bond is not large when chloroform is adsorbed on these supports. Indeed, all free hydroxyl groups on the Chromaton N Super surface are eliminated during silanization; the same groups are shielded by the modifier film on the modified support.

The oxygen-containing substances examined are much more polar than the chloro derivatives of hydrocarbons. Ethyl acetate, methyl ethyl ketone and *n*-propanol have different polarities and possibilities for hydrogen bond formation; however, when using the silanized support no marked differences in the molar heats of adsorption are observed for these substances. Moreover, although the dipole moment of the C = O bond is much higher than that of the C-Cl bond the molar heat of adsorption for methyl ethyl ketone is more positive (by about 20 kcal/mole) than that for dichloroethane. This indicates the high adsorption specificity of the Chromaton N Super surface and comparatively little influence of orientation forces on adsorption energy. The large difference in ΔH_a may reflect complex formation of the halogenated adsorbates with metal cations on the silanized support surface.

Comparing the molar heats of adsorption for the three oxygen-containing adsorbates, the greater difference is observed on the modified support: ethyl acetate and methyl ethyl ketone interact more strongly with the modified support surface than does *n*-propanol. Molecules of methyl ethyl ketone and of ethyl acetate have the same microdipole (C = O bond) moment which is higher than that of *n*-propanol (C-OH microdipole); therefore, the data for the modified support show that the orientation forces are the dominant specific (without taking into account dispersive forces) interaction on the surface. Free hydroxyl groups and any groups which can form the hydrogen bond are shielded on the modified support. Free hydroxyl groups at the ends of the Carbowax molecule seem to be bonded with the same groups on the support surface and the whole Carbowax molecule is bonded with the support surface by more stronger forces than physical adsorption. Only these strong bonds can be the reason for the good shielding of any active sites of the Chromaton surface. The data for the silanized support show the presence of hydrogen bonds with some active sites on the support surface when *n*-propanol is used as the adsorbate. Taking into account that all free hydroxyl groups on the silanized surface are converted into ethers, the presence of some non-hydroxyl groups on the surface which form hydrogen bonds is proved by the data.

Table II is of aid when considering intermolecular interactions between the

TABLE II

THERMODYNAMICS OF GAS-LIQUID DISTRIBUTION WHEN USING METHYLPOLYSILOXANE AS THE LIQUID AND BENZENE AS THE STANDARD

<i>Solute</i>	<i>r</i>	ΔH_s°	F^0
Carbon tetrachloride	1.033	0.18	-0.59
Chloroform	0.65	0.26	-0.40
Dichloroethane	0.83	0.08	-0.23
Methyl ethyl ketone	0.54	0.22	-0.84

silanized support and the adsorbates and in the solutions, the interactions in the solutions were determined by GLC. First, the differences in molar heats of solution are less than those in the molar heats of adsorption. The intermolecular interaction in the methylpolysiloxane solution occurs between the Si-CH₃ fragments of the stationary phase and the groups of the solute. When using the silanized support only part of the support surface is covered by -O-Si(CH₃)₃ groups, the main part being that of the initial calcinated surface of the diatomite. This is the reason for marked differences in interaction of the solution and the support.

Some information on the orientation of the sorbate molecules on the support surface may be obtained from F^0 data (F^0 mainly reflects loss of rotational entropy when the sorbate molecule passes from the gas phase to the support surface). The F^0 values on the modified support for all sorbates, except chloroform and dichloroethane, are smaller than that on the silanized support indicating that the surface of the modified support is more homogeneous³.

The A^* values for three adsorbates (the remaining ones have $A^* = 0$, i.e., exhibit linear adsorption isotherms) are given in Table III. An appreciable A^* value is

TABLE III

 A^* VALUES (RELATIVE UNITS) FOR SOME ADSORBATES ON CHROMATON N SUPER

<i>Adsorbate</i>	<i>Column temperature (°C)</i>		
	37.7	46.0	51.5
Methyl ethyl ketone	1.71	1.39	0.81
<i>n</i> -Propanol	1.69	1.43	1.06
Ethyl acetate	1.64	1.55	1.01

observed only on the silanized support which shows the greater non-homogeneity as compared with the modified support. The A^* values are about the same for all polar compounds studied indicating no preferable interactions for these adsorbates. Thus, such values serve as additional evidence of homogeneity of the compared support surfaces. These data are in good accord with suggestions^{4,5} about symmetrical peaks obtained for many polar substances on the Carbowax-modified support.

CONCLUSIONS

The experimental thermodynamic data allow us to make some conclusions on

the nature of the two supports. Even the most optimal silanization procedure does not yield a chemically inert and homogeneous surface, although free hydroxyls are eliminated. Some surface impurities (presumably, metal cations) on the silanized support determine the strong intermolecular interaction with some classes of adsorbates including bonds with π -electrons. The modifier film of thermally bonded Carbowax gives a homogeneous support surface of low polarity with no specific interactions with the adsorbate molecules.

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