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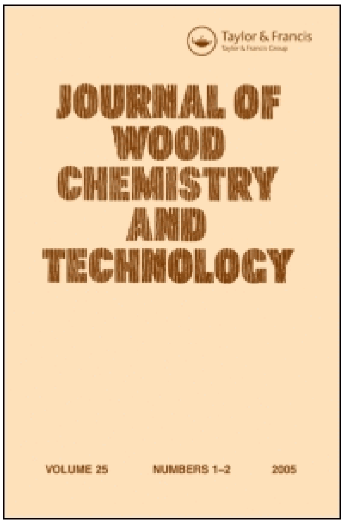

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# ANALYSIS OF THE ADSORPTION OF ALKANES ON HIGH SURFACE AREA CELLULOSE BY INVERSE GAS CHROMATOGRAPHY

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Dedicated to the memory of Kyosti V. Sarkanen

## ABSTRACT

The adsorption characteristics of alkanes on high surface area cellulose were investigated by inverse gas chromatography.

The enthalpy and entropy of adsorption of alkanes on the solvent exchanged cellulose were greater than the values on non-porous cellulose. The difference in the heats of adsorption of alkanes between the non-porous and the solvent exchanged cellulose was greater for larger molecules indicating stronger interaction for the higher alkanes in the pore structure. For n-hexane the differences in enthalpy and entropy of adsorption were 17 kJ/mole and 52 J/mole K, respectively. The London component of the surface free energy of adsorption was 116 mN/m for the solvent exchanged cellulose.

## INTRODUCTION

The adsorption of gases on cellulose has frequently been used to investigate fiber surface area and pore size distribution.[1-7] However, the gas adsorption method has not been employed as extensively to study the thermodynamics of adsorption. The change of the free energies of adsorption for nitrogen on cotton as a function of partial pressure was investigated by Rowen et al.[8] Haselton[3] determined the free energies and isosteric heats of adsorption as a function of surface coverage for nitrogen and butane on a variety of cellulose samples using a static adsorption method. Inverse gas chromatography has been used by Gray et al.[7,8] to study the thermodynamics of adsorption of n-alkanes on cellophane and cellulose. Lee and Luner studied both sized and unsized cotton papers.[9] However, these studies examined only low surface area cellulose samples ~1 to 2 $m^2/g$.

The adsorption of nitrogen on a fully bleached sulfite pulp, liquid-exchanged from its water-swollen (W) state to methanol (A) and finally with a nonpolar (N) liquid hydrocarbon, was studied by Merchant.[5] Type II adsorption isotherms with hysteresis loops were obtained for nitrogen on these WAN-dried fibers. The closure of the hysteresis loop occurred at $p/p_0$ values of 0.40 and 0.42. The maximum change of slope of the desorption curve occurred at $p/p_0 = 0.475$. The observation of hysteresis was attributed to the porous nature of the WAN-dried fibers. Barber[10] investigated the dependence of the adsorptive potential of the average patch of a heterogeneous surface for various cotton samples from the adsorption isotherms of argon gas. WAN-dried cotton (130 $m^2/g$) and water-dried cotton (1.41 $m^2/g$) showed 1.22 kcal/mole and 1.26 kcal/mole for the adsorption potential indicating only a minor dependence on the energy site distribution.

The adsorption isotherm on a porous solid differs from a non-porous solid since the adsorption in the pores is limited by their width. Type IV and V adsorption isotherms are generally observed on macroporous solids while Type I adsorption isotherms are obtained on microporous solids.[11-14] It is well-documented that when a solid contains micropores complications result in adsorption because the potential fields from opposite walls will overlap. This overlapping of attractive force acting on adsorbate molecules increases adsorption, thus affecting the thermodynamic parameters.[15,16]

To extend our understanding of the adsorption characteristics of cellulose, the adsorption of alkanes on high surface area cellulose were investigated at infinite dilution and finite concentration by inverse gas chromatography. The thermodynamic parameters of adsorption, $\Delta H$, $\Delta G$ and $\Delta S$, and the London component of the surface free energy of the solvent-exchanged cellulose will be discussed and contrasted to the earlier results obtained on low surface area cellulose.[9]

## RESULTS AND DISCUSSION

### Adsorption of Alkanes on Solvent-exchanged Cellulose at Infinite Dilution

The nitrogen flow rate was maintained at 14.1-14.8 mL/min. A decrease of the net retention volume was noticed at flow rates higher than 17.0 mL/min indicating nonequilibrium adsorption, but at flow rates between 11.5 - 16.5 mL/min fairly constant net retention volumes were obtained. The standard deviation of the net retention volume in this range of carrier gas flow rates was less than 0.6%. Symmetrical elution peaks were obtained, and their elution times were constant over a significant range of injected adsorbate volumes at this flow rate. These are good indications that the experiments were made in the Henry's law region. High alkanes gave broad peaks, especially at low temperatures, due to their strong interaction with the porous cellulose.

Henry's law constants, $K_S$, were calculated from the gas chromatography retention data according to Eq. [1] and are presented in Table 1.

$$K_S = \frac{V_N}{A} \qquad [1]$$

where $V_N$ is the net retention volume and A is the total surface area of the stationary phase. At least three net retention volumes were used to calculate each Henry's law constant.

The standard free energy of adsorption at infinite dilution, $\Delta G_A^o$, was calculated according to Eq. [2]

$$\Delta G_A^o = -RT \ln(K_S \times 2.99 \times 10^8) \qquad [2]$$

where R is the gas constant.

The standard enthalpy of adsorption at zero coverage, $\Delta H_A^o$, was calculated from the linear least squares slope of the plots of $\ln K_S$ against 1/T (See Figure 1) according to Eq. [3].

## TABLE 1

**Henry's Law Constant of Alkanes on Solvent Exchanged Cellulose**

| Adsorbate | $K_S \times 10^6$, m | | | |
|---|---|---|---|---|
| | 293°K | 298°K | 303°K | 308°K |
| n-pentane | 0.51 | 0.35 | 0.30 | 0.24 |
| n-hexane | 3.51 | 2.40 | 1.78 | 1.37 |
| 3-methylpentane | 2.16 | 1.37 | 1.11 | 0.87 |
| 2,2-dimethylbutane | 1.18 | 0.85 | 0.66 | 0.51 |
| 2,3-dimethylbutane | 1.64 | 1.24 | 0.90 | 0.70 |

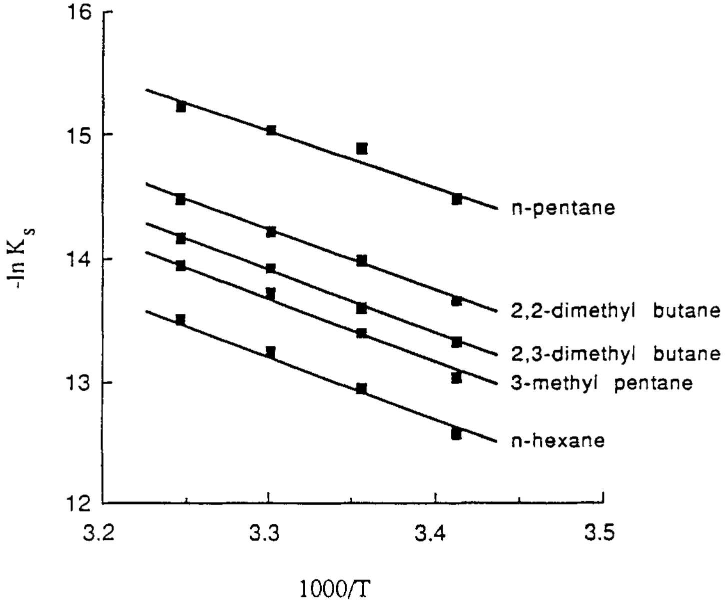

FIGURE 1. The variation of Henry's law constant with temperature for alkanes on solvent-exchanged cellulose.

$$\Delta H_A^o = -R \frac{d(\ln K_S)}{d(1/T)} \qquad [3]$$

The standard entropy of adsorption of the probes at infinite dilution, $\Delta S_A^o$, was obtained from the difference between $\Delta G_A^o$ and $\Delta H_A^o$ according to Eq. [4].

$$\Delta S_A^o = (\Delta H_A^o - \Delta G_A^o)/T \qquad [4]$$

The thermodynamic parameters for alkanes on solvent-exchanged cellulose surface obtained at zero surface coverage are shown in Table 1. The enthalpies of adsorption of n-pentane and n-hexane on the solvent-exchanged cellulose were higher than those on nonporous cellulose by 11 and 17 kJ/mole, respectively,[9] indicating stronger adsorbate-adsorbent interaction. Similarly, the entropies of adsorption for n-pentane and n-hexane on the solvent-exchanged cellulose were greater than the values obtained for nonporous cellulose by as much as 42 and 54 J/mole $^oK$. Since the adsorptive potential of solvent-exchanged cellulose is the same as that of nonporous cellulose[10], the differences in $\Delta H_A^o$ and $\Delta S_A^o$ values is in all probability the result of the presence of the pore structure.

The larger difference between the two substrates in the enthalpy of adsorption for n-hexane than for n-pentane indicates the greater effect of pores on the adsorption of n-hexane. This is due to more efficient pore filling by the larger n-hexane which make it interact more favorably with the long-ranged nature of the dispersion component overlapped in the micropores.

## TABLE 2

**Standard Thermodynamic Data for the Zero Coverage Adsorption of Alkanes on Solvent Exchanged Cellulose at 30°C**

| Adsorbate | $-\Delta G_A^o$ (kJ/mole) | $-\Delta H_A^o$ (kJ/mole) | $-\Delta S_A^o$ (J/mole °K) |
|---|---|---|---|
| n-pentane | 11.29 | 36.14 | 81.99 |
| n-hexane | 15.82 | 46.92 | 102.65 |
| 3-methylpentane | 14.63 | 44.19 | 97.55 |
| 2,2-dimethylbutane | 13.32 | 41.58 | 93.27 |
| 2,3-dimethylbutane | 14.10 | 42.99 | 95.34 |

Kiselev et al.[16] investigated the effect of the geometrical structure of silica gels on the gas chromatograph of hydrocarbons and found that the narrowing of pores increases the heats of adsorption, particularly for high alkanes. The heats of adsorption decreased drastically as the average pore diameter increased from 22 to 70 Å, which suggests the operative distance of the nonspecific interaction.[16]

The thermodynamic parameters for the other hexane isomers fell between those for n-pentane and n-hexane. This is probably due to the compact shape of the isomers which reduces the interaction with the surface. Maximum interaction occurs when the n-alkane molecules adsorb on the surface with a stretched conformation, which allows for a maximum number of direct contacts.

A linear relationship between the thermodynamic parameters of adsorption and the number of methylene groups has been observed earlier[9] and this relationship was applied to obtain the London component of the surface free energy[6,7]. However, on the porous cellulose column only n-pentane and n-hexane showed good gas chromatographic peaks, which could be used for the thermodynamic calculations. Due to the low flow rate employed, broad chromatographic peaks for n-alkanes higher than n-hexane resulted in low peak heights indistinguishable from the base line even at the highest sensitivity of the FID detector. Therefore, the linear relationship between the thermodynamic parameters and the number of carbon atoms in n-alkanes could not be confirmed over a wider range. However, by plotting $\Delta G_A^o$ against log $p_0$ ($p_0$ = saturated vapor pressure) for n-pentane, n-hexane, and the hexane isomers, a linear relationship was observed as shown in Figure 2. This suggests that $\Delta G_A^o$ is proportional to the number of carbon atoms in n-alkanes and not their location.

The London component of the surface free energy of the solvent exchanged cellulose was calculated by Eq. 5.[6]

$$\frac{-\Delta G_A^o(CH_2)}{N\ a(CH_2)} = 2(\gamma(CH_2)\ \gamma_S^L)^{1/2} \qquad [5]$$

where $\Delta G_A^o(CH_2)$, is the incremental standard fee energy of adsorption per mole of methylene group, $a(CH_2)$ is the area occupied by a methylene group on the surface, $\gamma(CH_2)$ is the surface tension of a hypothetical methylene liquid, $\gamma_S^L$ is the London component of the surface free energy of the stationary phase, and N is Avogadro's number.

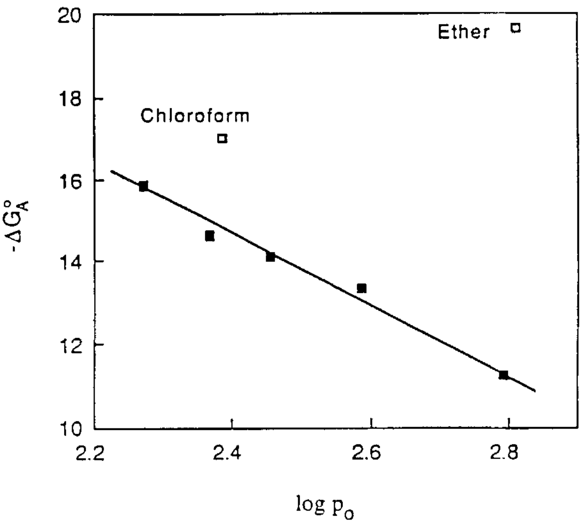

FIGURE 2. The standard free energy of adsorption vs. saturated vapor pressure of various alkanes.

Using the data from pentane and hexane, the London component of the surface free energy for porous cellulose was calculated (Table 3). The London component of surface free energy for solvent exchanged cellulose is extremely high. Similar values of $\gamma_S^L$ were determined for various metals such as tin, iron, lead and ferric oxide.[17] Most organic materials are, however, low energy solids. Many polymers exhibit London components of the surface free energy less than 50 mN/m. For cellulose it ranges from 40 to 49 mN/m depending on the cellulose sample preparation and experimental methods.

The very high London component values can be explained in several ways. First, the overlapping of the force field in narrow micropores and the size of the alkanes reducing the gap between the molecule and side wall of the pores may result in a high

**TABLE 3**

**The London Component of Surface Free Energy for Solvent Exchanged Cellulose**

| Temp. ($^{0}$K) | $\Delta G_{A}^{o}(CH_2)$ (kJ/mole) | $\gamma(CH_2)$ (mN/m) | $\gamma_S^L$ (mN/m) |
|---|---|---|---|
| 293 | 4.69 | 35.64 | 118.05 |
| 298 | 4.80 | 35.35 | 125.07 |
| 303 | 4.52 | 35.06 | 111.87 |
| 308 | 4.43 | 34.77 | 108.24 |

Average = 115.81

Std. Dev. = 7.38

London components of the surface free energy. Second, the slow effusion of n-hexane may contribute to the high London component. The constant retention volume observed at flow rates between 11.5 and 16.5 mL/min excludes the diffusion artifacts such as a deeper penetration of smaller molecules into the microcapillary structure. However, larger retention volumes for the higher alkanes may have been obtained, not because of the stronger adsorption on the surface, but because of the slow diffusion in the pores. According to Graham's law, at a constant temperature and at a constant pressure drop, the rates of effusion of various gases are inversely proportional to the square roots of their densities. When the slow effusion is considered, the retention time of n-hexane needs to be corrected by multiplying by 0.915. However, this only accounts for less than 10% of the high London component. Finally, the high values of the London components may originate from the limitations of Eq. [5]. In that equation only a two-dimensional surface contact is accounted for so that for n-alkanes $a(CH_2)$ is equal to 0.06 $nm^2$. In a micropore the contact area for a methylene group may be higher than on a flat surface. However, this can be regarded as another aspect of an overlapping force field in a micropore structure. The high London component of the high surface area cellulose can therefore be attributed mainly to the overlapping of the force field in a micropore.

The results for two polar adsorbates, diethyl ether and chloroform, are shown in Figure 2. The specific interaction for these polar probes was close to the values of nonporous cellulose. This suggests that the small polar probes do not experience the effect of pores. Kiselev _et al_.[16] found that narrowing of silica gel pores led to an increase in the heat of adsorption of large-sized organic molecules and produced a weaker effect on the adsorption of small polar or quadruple molecules.

## _Adsorption of n-Hexane in the Finite Region_

The porous cellulose adsorbent showed higher heats of adsorption than the nonporous cellulose at zero coverage. The heat of adsorption is the main factor determining the adsorption at a given relative pressure. The greater the heat of adsorption, the greater the amount adsorbed in the monolayer region, and the sharper the knee on the isotherm.

To study the effect of cellulose pore structure on the adsorption isotherm, chromatograms of n-hexane were obtained at finite concentration. Two adsorption isotherms were obtained at 10 and 30°C by injecting various amounts of n-hexane. The maximum amount of adsorbate which could be injected was 4.5μL and 3.5μL at 10°C and 30°C, respectively. A small void volume in the column prevented larger injection volumes. This in turn limited the range of the adsorption isotherm obtainable from inverse gas chromatography. The chromatograms and peak maxima envelopes are shown in Figure 3.

The chromatograms showed a rather sharp front and extended tail. The front sides of the chromatograms were not as vertical as those observed on the nonporous cellulose and AKD-sized paper.[9] At low injection levels the front sides were more diffuse. These shapes display the effects of slow equilibrium in the column. Another indication of a slow equilibrium can be found on the diffuse side which does not coincide for different injection volumes. However, the divergence was smaller for the solvent exchanged cellulose column than for cellophane[8] and porous silica.[16]

The peak maxima method was used to obtain the adsorption isotherm from the chromatograms. Eq. [6] and [7] were used to calculate the amount of adsorbate adsorbed per unit area of adsorbent, q, and the partial pressure of solute, p,

$$q = \frac{n_{cal} S_{ads}}{A\, S_{cal}} \qquad [6]$$

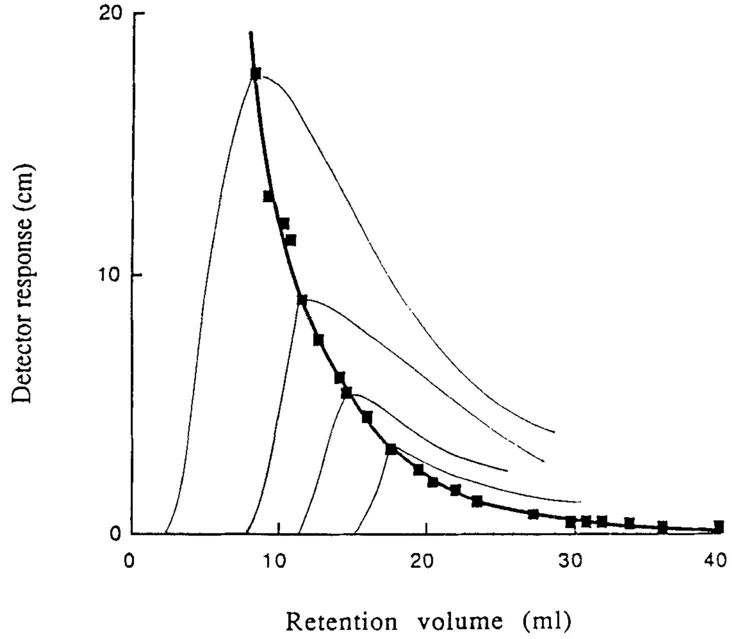

FIGURE 3. Gas chromatograms of n-hexane on solvent exchanged cellulose column at 30°C.

$$p = \frac{n_{cal}XRT}{S_{cal}F_{col}} \qquad [7]$$

where $S_{ads}$ is the area measured on the strip chart, $n_{cal}$ is the number of moles of solute injected for calibration, $S_{cal}$ is the total area under the calibration peak on the strip chart, A is the total surface area of stationary phase, X is the recorder chart speed, and $F_{col}$ is the carrier gas volume flow rate at column temperature T corrected for pressure drop and for the presence of water in the soap bubble meter. The area bounded by the GC adsorption envelope of the peak maxima, the gas hold-up time and a given detector response h is used for $S_{ads}$.

The adsorption isotherms of n-hexane are shown in Figure 4. For comparison, an adsorption isotherm of n-decane on nonporous cellulose is also shown in Figure 4. The n-decane isotherm is very similar to the n-hexane adsorption isotherm[29]. It appears that the adsorption isotherm difference between porous and nonporous cellulose is significant. Solvent exchanged cellulose shows a stronger adsorption tendency than nonporous cellulose.

Even though the entire adsorption isotherm was not obtained, the BET parameter, C, and the specific surface area were calculated from the isotherms. A higher C value was obtained for solvent exchanged cellulose which is related to the knee sharpness of the isotherm and stronger interaction between adsorbate and adsorbent. C values of 8.6 and 12.5 were obtained for adsorption isotherms at 10°C and 30°C, respectively. For decane on nonporous cellulose it ranged from 6.0 to 6.4[9]. The specific surface areas obtained from the isotherms were 68.4 $m^2/g$ and 47.2 $m^2/g$ at 10°C and 30°C, respectively. The specific surface area obtained at 10°C agrees well with the value obtained by nitrogen adsorption. However, the surface area obtained at 30°C was significantly lower. The reason for this difference may be due to structural changes occurring during the repeated adsorption and desorption of n-hexane at 10°C which caused the micropores to be closed. The experiments at 30°C itself may have induced pore collapse leading to a lower surface area. Residue adsorption of n-hexane i.e. filled pores, may also

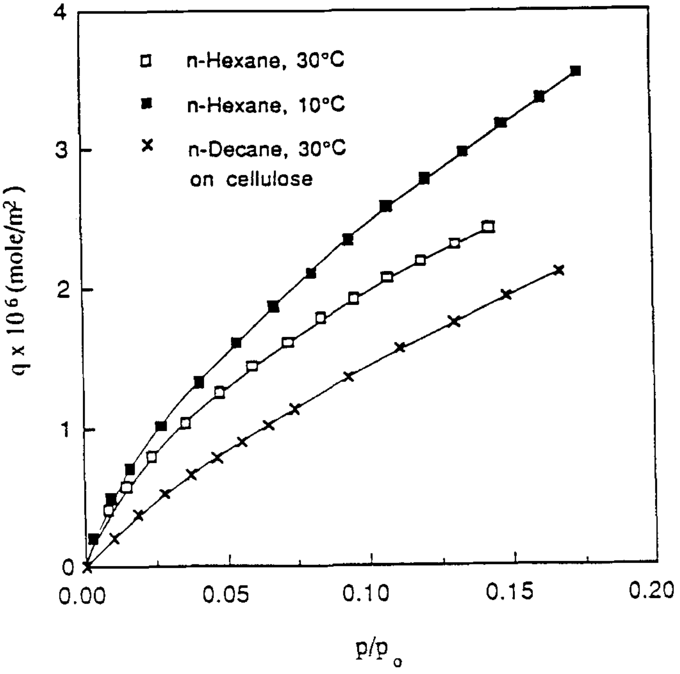

FIGURE 4. Adsorption isotherms of n-hexane on solvent exchanged cellulose and n-decane on cellulose.

be responsible for the lower surface area. Only further experiments could resolve this question.

## EXPERIMENTAL

### Stationary Phase and Column Preparation

Confetti of Whatman No. 1 filter paper were prepared by passing strips through a clean-telex punch machine. The confetti was swollen in water for two days. The water in the confetti was exchanged with ethyl alcohol, which was subsequently exchanged with acetone. The acetone was replaced with toluene and finally, the tolune was exchanged with n-heptane. The confetti was kept in each solvent for two days and was replaced twice with fresh solvent. The n-heptane was evaporated by holding the sample in a vacuum oven at 105$^{\circ}$C for three days.

The BET nitrogen surface area was measured with a Quantasorb adsorption apparatus. The BET area of the solvent exchanged cellulose confetti was 64.58 $m^2/g$.

Solvent exchanged cellulose was packed into copper tubing with an outer diameter of 0.25 in. The weight of the stationary phase was 0.128 g. To reduce the dead volume, 0.125 in stainless steel tubing was used to mount the column onto the gas chromatograph.

### Apparatus

A Varian 1740 Gas Chromatograph with two flame-ionization detectors (FID) was used to measure retention volume. A detailed description of the gas chromatograph is given elsewhere.[9] Briefly the column oven was replaced with a water bath to control the column temperature more accurately and to make subambient runs. The temperature of the water bath was controlled by circulating water at a constant temperature. The injector and detector temperature were set at 120 and 250$^{\circ}$C, respectively. The nitrogen flow rate was 14.1-14.8 mL/min.

### Adsorbates

The adsorbates (n-pentane, n-hexane, 2,2-dimethylbutane, 2,3-dimethylbutane, and 3-methylpentane) were obtained from Aldrich Chemical Co. and used without further purification. Retention data were recorded on a Fisher Recordall 5000 chart recorder. For the infinite dilution experiments, trace amounts of vapors were injected from a Hamilton gas-tight syringe. The highest sensitivity of the detector was employed for these experiments. In the finite concentration region, various amounts of liquid adsorbates were injected. Due to the low boiling point of n-hexane and small void volume in the column, 3.5 and 4.5 μL were the maximum amounts which could be injected without blowing out the flame in the FID detector at 30°C and 10°C, respectively.

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