

## Use of a gamma energy distribution to model the gas chromatographic temperature dependence of solute retention on aryl-siloxane chemically modified porous carbon

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### ABSTRACT

A new equation is derived for the corrected specific retention volume of an infinitely dilute solute on an energetically heterogeneous surface. The equation, which is based on a gamma-type distribution for the adsorption energy, is used to model the temperature dependence of the specific retention volume for benzene chromatographed on four different chemically modified porous carbon adsorbents. Biphasic behavior in plots of the  $\ln V_{s,t}$  vs.  $1/T$  are interpreted in terms of differing energetic heterogeneities of the modified carbons.

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### INTRODUCTION

Since it is well-known that surface heterogeneity, especially under dilute conditions, substantially influences the adsorption process<sup>1</sup>, gas-solid chromatography (GSC), which permits measurements to be made at low concentrations<sup>2</sup>, is an attractive technique for studying surface and structural differences of adsorbents and catalysts<sup>3</sup>. Although many investigators<sup>4–8</sup> have used both temperature- and concentration-dependent retention measurements to characterize surface heterogeneity, further theoretical and experimental studies via GSC are important in order to develop additional numerical models which may be used to describe surface and structural heterogeneities of solids.

In the current paper a simple equation is derived using a gamma-type distribution to describe the surface adsorption energy heterogeneity. Additionally this relationship has been used to model the temperature dependence of retention data for benzene chromatographed on four different chemically modified porous carbons. It has been shown that this simple equation can be used to explain two linear segments of the temperature-dependent retention curves which have different slopes and occur in the temperature range from 363 K to 458 K.

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## THEORY

For an infinitely dilute solute in the gas (mobile) phase the corrected specific retention volume,  $V_s$ , at a column temperature  $T$  (K) is equal to the distribution constant  $K_c$  (refs. 9 and 10):

$$V_s = K_c \equiv c_s/c_g \quad (1)$$

where  $c_g$  expressed in mol/ml is the equilibrium solute concentration in the mobile (gas) phase and  $c_s$  expressed in mol/m<sup>2</sup> is the equilibrium solute concentration on the stationary (surface) phase. Using  $c_s^0$  to denote the maximum solute concentration on the surface and  $\theta = c_s/c_s^0$  to describe relative coverage eqn. 1 may be rewritten such that:

$$V_s = c_s^0 K \quad (2)$$

where  $K = \theta/c_g$ . The distribution constant  $K$  also may be expressed as follows<sup>5</sup>:

$$K = \alpha \exp(\varepsilon/RT) \quad (3)$$

where  $\varepsilon$  is the adsorption energy of a solute,  $R$  is the universal gas constant, and  $\alpha$  is the temperature-dependent entropy factor<sup>11</sup>.

For a heterogeneous surface containing  $L$  types of adsorption sites the total specific retention volume,  $V_{s,t}$ , of a solute is the sum of the specific retention volumes,  $V_{s,l}$ , arising from all types of adsorption sites. This relationship is given in eqn. 4

$$V_{s,t} = \sum_{l=1}^L V_{s,l} \quad (4)$$

where  $V_{s,l}$  denotes the individual specific retention volumes for the 1, 2, ...,  $L$  ( $l$ th) type of adsorption sites. Taking into account eqns. 2 and 3,  $V_{s,l}$  may be expressed as follows:

$$V_{s,l} = \alpha c_{s,l}^0 \exp(\varepsilon_l/RT) \quad (5)$$

where  $c_{s,l}^0$  and  $\varepsilon_l$  denote respectively the maximum solute concentration and adsorption energy. In developing eqn. 5 it is assumed that the entropy factor,  $\alpha$ , is independent of the type of adsorption sites. This assumption has been commonly used in developing other gas adsorption models for energetically heterogeneous solids<sup>1</sup>.

Eqn. 4 may be rewritten to the following:

$$V_{s,t} = \alpha c_{s,t}^0 \sum_{l=1}^L f_l \exp(\varepsilon_l/RT) \quad (6)$$

where

$$f_l = c_{s,l}^0/c_{s,t}^0 \quad (7)$$

and

$$c_{s,t}^0 = \sum_{i=1}^L c_{s,i}^0 \quad (8)$$

In the above relationship  $f_i$  is the fraction of adsorption sites of the  $i$ th type and  $c_{s,t}^0$  is the maximum solute concentration for the total surface.

In cases where a large number of different types of adsorption sites exist ( $L \rightarrow \infty$ ), the summation used in eqn. 6 to define a finite number may be replaced by an integration. After doing this eqn. 9 is obtained

$$V_{s,t} = \alpha c_{s,t}^0 \int_{\Delta} \exp(\varepsilon/RT) F(\varepsilon) d\varepsilon \quad (9)$$

where the distribution function of the adsorption energy  $F(\varepsilon)$  satisfies the following normalization condition:

$$\int_{\Delta} F(\varepsilon) d\varepsilon = 1 \quad (10)$$

over an the integration region  $\Delta$ .

Eqn. 9 describes the total specific retention volume  $V_{s,t}$  of a infinitely dilute solute chromatographed on an energetically heterogeneous surface with a distribution of adsorption sites. Although this equation may be integrated for different assumed distributions of the adsorption energy, it has been shown elsewhere<sup>1,12</sup> that a gamma-type function is a good mathematical model for describing the behaviour of many heterogeneous surfaces. This function for  $\varepsilon > \varepsilon_m$  is given in eqn. 11

$$F(\varepsilon) = [\rho^\gamma / \Gamma(\gamma)] (\varepsilon - \varepsilon_m)^{\gamma-1} \exp[-\rho(\varepsilon - \varepsilon_m)] \quad (11)$$

where  $\varepsilon_m$  is the minimum adsorption energy,  $\gamma$  and  $\rho$  are parameters greater than zero, and  $\Gamma$  is the gamma special function. For  $0 \leq \gamma \leq 1$  the gamma distribution is an exponentially decreasing relationship and for  $\gamma > 1$  it is an asymmetrical single-peak with a maximum at:

$$\varepsilon_0 = \varepsilon_m + (\gamma - 1)/\rho \quad (12)$$

The parameters  $\rho$  and  $\gamma$  are associated with the average adsorption energy  $\varepsilon^5$ , where  $\varepsilon^* = \gamma/\rho$  (eqn. 13) and its dispersion  $\sigma$  (eqn. 14).

$$\bar{\varepsilon} = \varepsilon_m + \varepsilon^* \quad (13)$$

and

$$\sigma = \gamma^{1/2}/\rho \quad (14)$$

The quantities  $\bar{\varepsilon}$  and  $\sigma$  in eqns. 13 and 14 have a clear physical meaning;  $\bar{\varepsilon}$  denotes the average adsorption energy, whereas  $\sigma$  denotes the dispersion in the energy distribution function  $F(\varepsilon)$ .  $\bar{\varepsilon}$  provides information about position of the distribution function  $F(\varepsilon)$  on the energy axis, whereas,  $\sigma$  reflects its width (*i.e.*, energy range). Also, a comparison of  $\bar{\varepsilon}$  with  $\varepsilon_0$  provides information about the asymmetry of  $F(\varepsilon)$ . For  $\varepsilon_0 = \bar{\varepsilon}$  the function  $F(\varepsilon)$  is symmetrical, whereas for  $\bar{\varepsilon} > \varepsilon_0$  it is asymmetrical in the direction of high values of  $\varepsilon$ , and for  $\bar{\varepsilon} < \varepsilon_0$  it is asymmetrical in the opposite direction.

Presented in Fig. 1 for illustrative purposes are a series of  $F(\varepsilon)$  curves generated for the case where  $\varepsilon^* = 2.1$  kJ/mol. Larger values of  $\sigma$  and  $\varepsilon^*$  are obtained for more heterogeneous surfaces and the energy distribution function  $F(\varepsilon)$  is skewed in the high-energy direction.

Substitution of eqn. 11 into eqn. 9 gives:

$$V_{s,t} = [\alpha c_{s,t}^0 \rho^\gamma / \Gamma(\gamma)] \int_{\varepsilon_m}^{\infty} (\varepsilon - \varepsilon_m)^{\gamma-1} \exp(\varepsilon/RT) \exp[-\rho(\varepsilon - \varepsilon_m)] d\varepsilon \quad (15)$$

Because the gamma distribution,  $F(\varepsilon)$ , approaches zero as  $\varepsilon$  goes to infinity, the upper integration limit in eqn. 15 is set at  $\infty$ . Introducing the new variable  $E = \varepsilon - \varepsilon_m$  into eqn. 15:

$$V_{s,t} = [\alpha c_{s,t}^0 \rho^\gamma \exp(\varepsilon_m/RT) / \Gamma(\gamma)] \int_0^{\infty} E^{\gamma-1} \exp[-(\rho - 1/RT)E] dE \quad (16)$$

After integration:

$$V_{s,t} = \alpha c_{s,t}^0 (1 - 1/\rho RT)^{-\gamma} \exp(\varepsilon_m/RT) \quad (17)$$

or

$$V_{s,t} = V_{s,m} (1 - 1/\rho RT)^{-\gamma} \quad (18)$$

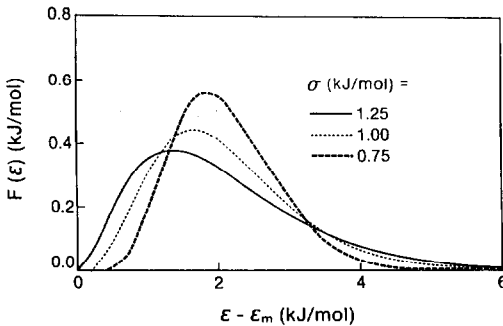


Fig. 1. Adsorption energy distributions calculated according to eqn. 11 for  $\varepsilon^* = 2.1$  kJ/mol and different values of  $\sigma$ .

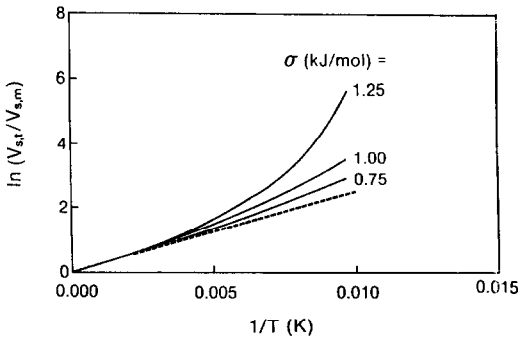


Fig. 2. Dependences of the logarithm of the relative retention volume  $V_{s,t}/V_{s,m}$  against reciprocal of temperature associated with the adsorption energy distributions shown in Fig. 1. The dashed line represents the high temperature limit of eqn. 20, which is given by eqn. 21.  $\epsilon^* = 2.1$  kJ/mol.

where

$$V_{s,m} = \alpha c_{s,t}^0 \exp(\epsilon_m/RT) \quad (19)$$

$V_{s,m}$  in eqns. 18 and 19 is the specific retention volume associated with the adsorption site with minimum energy,  $\epsilon_m$ . Thus the influence of an adsorbent's heterogeneity on  $V_{s,t}$  is described by the expression  $(1 - 1/\rho RT)^{-\gamma}$ . This relationship is illustrated in Fig. 2 where  $\ln(V_{s,t}/V_{s,m})$  is plotted against the reciprocal of temperature according to the following equation:

$$\ln(V_{s,t}/V_{s,m}) = -\gamma \ln(1 - 1/\rho RT) \quad (20)$$

For small values of  $1/\rho RT$  eqn. 20 may be approximated as follows:

$$\ln(V_{s,t}/V_{s,m}) = \gamma/\rho RT = \epsilon^*/RT \quad (21)$$

For  $\epsilon^* = 2.1$  kJ/mol. The dotted line in Fig. 2 represents linear fits according to eqn. 21, whereas the solid lines were calculated according to eqn. 20 for the values of the energy distributions function shown in Fig. 1 (*i.e.*,  $\sigma = 0.75, 1.00$  and  $1.25$  kJ/mol). From Fig. 2 it can be seen that at lower temperatures an adsorbent's heterogeneity influences strongly the temperature dependence of the specific retention volume (*i.e.*, a significant deviation of the solid curves from the dotted straight line). However, this deviation decreases when the surface heterogeneity,  $\sigma$ , decreases. At higher temperatures where the solid curves and the dotted line is nearly superimposable changes in  $\sigma$  do not influence significantly the temperature-dependence of  $V_{s,t}$ . A characteristic feature of each of the curves in the higher temperature region is linearity with a slope equal to  $\epsilon^*/R$ . Thus, the adsorbent's heterogeneity is reflected in the parameters  $\gamma$  and  $\rho$ , which influence the slope,  $\epsilon^*/R$ , of the linear temperature dependence of  $V_{s,t}$  shown in Fig. 2.

If eqn. 17 is rewritten in logarithmic form, we obtain

$$\ln V_{s,t} = \ln(\alpha c_{s,t}^0) + \epsilon_m/RT - \gamma \ln(1 - 1/\rho RT) \quad (22)$$

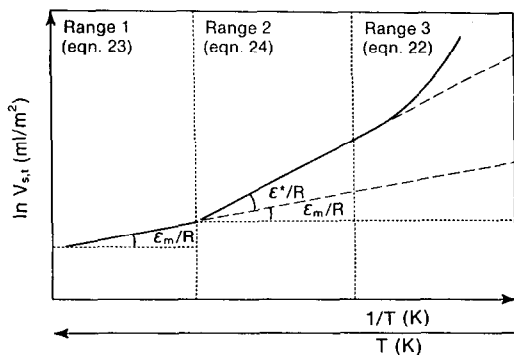


Fig. 3. A schematic representation of the dependence of the logarithm of the specific retention volume on reciprocal of temperature of a heterogeneous solid.

The first term in the above expression is related to the entropy effect in GSC, the second term provides information about the minimum adsorption energy, and the third term describes the effect of adsorbent heterogeneity on the specific retention volume. The temperature dependence of the first term in comparison to the other terms is negligible<sup>11</sup>.

At higher temperatures  $1/\rho RT$  is nearly zero and the third term in eqn. 22 may be neglected. Under these conditions eqn. 22 is reduced to a linear relationship (eqn. 23) with a slope of  $\epsilon_m/R$ .

$$\ln V_{s,t} = \ln(\alpha c_{s,t}^0) + \epsilon_m/RT \quad (23)$$

For the intermediate temperatures the third term of eqn. 22 can be approximated by eqn. 21 and a new linear expression is obtained (eqn. 24).

$$\ln V_{s,t} = \ln(\alpha c_{s,t}^0) + \epsilon_m/RT + \epsilon^*/RT = \ln(\alpha c_{s,t}^0) + \bar{\epsilon}/RT \quad (24)$$

in which the third term can be approximated by  $\epsilon^*/RT$ . In this second temperature range a higher value for the slope is obtained compared to that at higher temperatures.

The above conditions are illustrated schematically in Fig. 3. Range 1 corresponds to higher temperatures where  $1/\rho RT$  is assumed to be zero (eqn. 23). Range 2 corresponds to intermediate temperatures where  $1/\rho RT$  is small but non-negligible (eqn. 24) and range 3 corresponds to lower temperatures where all terms in eqn. 22 must be considered. In this latter region  $\ln V_{s,t}$  vs.  $1/T$  deviates significantly from linearity. The degree of deviation depends strongly on the adsorbent heterogeneity (*i.e.*, the  $\sigma$  value as illustrated in Fig. 2).

Thus, in summary, eqn. 22 can be utilized to model retention behavior over a broad range of temperatures. Mathematical analysis of this expression shows that at higher and intermediate temperatures simplified versions (respectively, eqns. 23 and 24) can be used to describe the linear behavior of  $\ln V_{s,t}$  vs.  $1/T$ . At higher temperatures (range 1) little information is provided about adsorbent heterogeneity, only an estimate of the minimum adsorption energy,  $\epsilon_m$ . However, the increase in the slope of

the linear plot of  $\ln V_{s,t}$  vs.  $1/T$  observed for intermediate temperatures (range 2) is related to the adsorbent's heterogeneity. This increase is equal to:

$$\varepsilon^*/R = \bar{\varepsilon}/R - \varepsilon_m/R \quad (25)$$

The first and second terms of eqns. 25 are respectively the slopes from the linear fits of range 2 and range 1. It can be seen from eqn. 13 that  $\varepsilon^*$  depends on the parameters  $\gamma$  and  $\rho$ , which characterize the gamma energy distribution function  $F(\varepsilon)$  (eqn. 11). Fig. 2 shows that range 2 is expected to be wider for more heterogeneous cases. A further characteristic of range 2 is an independence of the slope on the dispersion,  $\sigma$ . Thus, range 2 provides an estimate of  $\varepsilon^*$ , a measure of the adsorbent heterogeneity.

A more complete picture of the surface heterogeneity can be obtained by studying  $V_{s,t}$  over a wide range of temperatures, which include experimental measurements in ranges 1, 2 and 3. Fig. 2 also illustrates that the deviations from linearity in the curves is a measure of the dispersion,  $\sigma$ . If the deviation is large, then  $\sigma$  is also large. Thus, range 3 provides information about the dispersion,  $\sigma$ , of the energy distribution function.

## EXPERIMENTAL

### *Chemically modified porous carbons*

Porous chromatographic grade carbon (Carbopack B) from Supelco (Bellefonte Park, PA, U.S.A.) with an approximate surface area of  $100 \text{ m}^2/\text{g}$  was used to prepare four types of chemically modified adsorbents. This was carried out by first reacting the Carbopack B with 3-aminopropyltriethoxysilane (AS) in the presence of a primary amine. Subsequently, the AS-carbon was modified further by treatment with one of four different arylacid chlorides, 3,5-dinitrobenzoyl chloride (DNBA), 4-nitrobenzoyl chloride (PNBA), 4-methylbenzoyl chloride (PMBA), and benzoyl chloride (BA). More exact details concerning preparation of the chemically modified porous carbons are given elsewhere<sup>13</sup>.

A schematic representation of the attached functional groups on the carbon is shown in Fig. 4. The four chemically modified porous carbons are referred to throughout the remainder of the text as: AS-DNBA, AS-PNBA, AS-PMBA and AS-BA. All solvents used in preparation of these materials were reagent grade. The 3-aminopropyltriethoxysilane was obtained from Petrarch Systems (Levittown, PA, U.S.A.) and DNBA, PNBA, PMBA and BA were from Aldrich (Milwaukee, WI, U.S.A.).

### *Chromatographic measurements*

Since the surface properties of porous carbons are frequently characterized using benzene as a test adsorbate<sup>14</sup>, benzene also was used in the current study as a test solute. Before making retention measurements, each of the modified carbons, about 0.15 g, was dry packed into a stainless-steel column,  $10 \text{ cm} \times 3.2 \text{ mm}$  I.D. Pressure drop and void volume measurements were made as described elsewhere<sup>13</sup>.

All gas chromatographic measurements were carried out using a Shimadzu model Mini-2 gas chromatograph with a flame ionization detector using nitrogen as the carrier gas. Retention times were recorded by a Hewlett-Packard Model 3393A

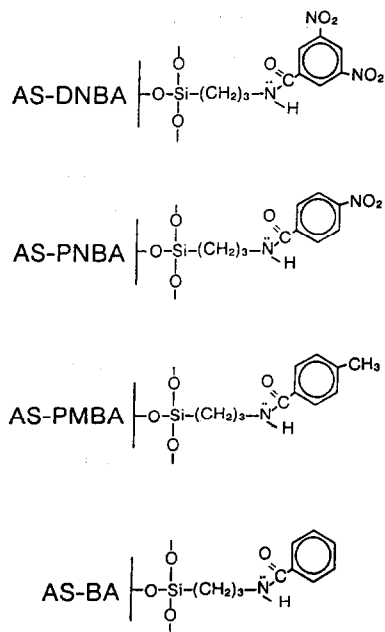


Fig. 4. Surfaces of modified porous carbon prepared by attachment of different benzamide ligands.

integrator. Each retention measurement represents the average of at least two injections and each column was studied twice to determine reproducibility of the measurements.

## RESULTS AND DISCUSSION

Shown in Fig. 5 are plots of  $\ln V_{s,t}$  vs.  $1/T$  for benzene chromatographed on columns packed with the AS-DNBA, AS-PNBA, AS-PMBA and AS-BA carbons. Over the temperature range studied, 363–458 K, the experimental dependence of  $\ln V_{s,t}$  vs.  $1/T$  are approximated by two linear segments, with intersection points from about 398 K for AS-PNBA and AS-BA, and about 423 K for AS-DNBA and AS-PMBA. If it assumed that the linear segments in Fig. 5 at the higher temperatures (low values of  $1/T$ ) correspond to range 1 in Fig. 3 and at lower temperatures (higher values of  $1/T$ ) are related to range 2 in Fig. 3, then these data may be interpreted in terms of eqns. 23 and 24, respectively. Summarized in Table I are calculated values of  $\epsilon_m$  and  $\epsilon^*$ , studied. The highest value of  $\epsilon_m$  was obtained for the AS-PNBA adsorbent and decreased in the order: AS-PNBA > AS-BA > AS-DNBA > AS-PMBA.

All four of the materials studied were prepared via chemical modification of the same porous carbon which consists of twisted aromatic sheets with a number of different types to exposed oxygen groups<sup>15</sup>. During chemical modification a portion of the surface oxygen groups were silanized and then modified by attaching selected benzamide groups: PNBA, BA, DNBA or PMBA. Thus, each of the modified carbons possesses a similar set of unmodified groups or patches plus a selected type of



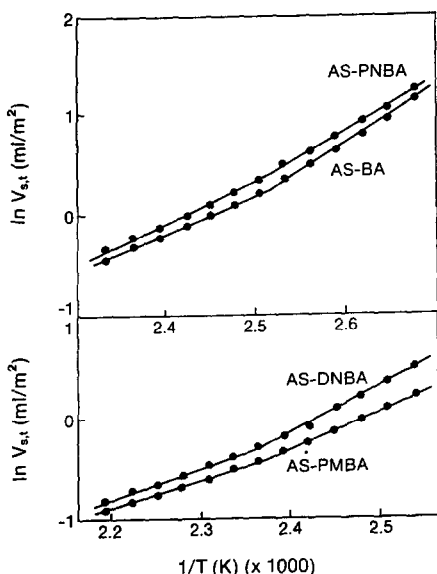


Fig. 5. Experimental dependences  $\ln V_{s,t}$  vs.  $1/T$  for benzene on four modified porous carbons. The solid lines show linear segments of these dependences.

arylamide group. If the minimum adsorption energy,  $\epsilon_m$ , represented the interaction of benzene with the unreacted patches, the values of  $\epsilon_m$  should have been identical for all of the modified carbons. This was found not to be the case as seen by the data in Table I. Rather, since the values of  $\epsilon_m$  were dependent on surface modification, it seems reasonable to infer that they reflect the interaction energy between benzene and the various bonded aryl-ligands. Based on this premise, the strongest interaction was observed for benzene with the PNBA ligand, whereas, the weakest was observed for benzene with the PMBA ligand. The interactions between benzene and the BA and

TABLE I

ADSORPTION ENERGY PARAMETERS EVALUATED FROM TWO LINEAR SEGMENTS OF THE EXPERIMENTAL DEPENDENCE  $\ln V_{s,t}$  VS.  $1/T$  FOR BENZENE CHROMATOGRAPHED ON FOUR SAMPLES OF MODIFIED POROUS CARBONS

For AS-PNBA and AS-BA the linear segments were drawn at the 363–388 and 408–423 K temperature ranges, whereas for AS-DNBA and AS-PMBA these linear segments were drawn at the 388–413 and 433–458 K temperature ranges.

Modified carbon	Minimum adsorption energy, $\epsilon_m$ (kJ/mol)	Additional average energy generated by surface heterogeneity, $\epsilon^*$ (kJ/mol)
AS-PNBA	$32.6 \pm 0.8$	$5.9 \pm 3.8$
AS-BA	$28.0 \pm 0.8$	$13.0 \pm 5.0$
AS-DNBA	$27.6 \pm 1.3$	$10.5 \pm 1.3$
AS-PMBA	$22.6 \pm 1.7$	$8.4 \pm 2.5$

DNBA ligands were intermediate. In the case of the simple aromatic and mono substituted aromatic ligands the order of  $\epsilon_m$  is consistent with simple ring inductive effects, where the pi-electron density for the ring decreases in the order of PMBA > BA > PNBA.

The second quantity reported in Table I is  $\epsilon^*$ . The values of  $\epsilon^*$  were calculated according to eqn. 21 from the linear fits of the  $\ln V_{s,t}$  vs.  $1/T$  plots associated with temperatures below 400 K. Based on theoretical considerations discussed earlier,  $\epsilon^*$  should reflect differences in surface heterogeneities between the modified adsorbents. For a heterogeneous surface with a distribution of sites with energy higher than the minimum adsorption energy,  $\epsilon_m$  the value of the  $i$ th adsorption site is  $\epsilon_i$  and the value  $\epsilon_{im} \equiv \epsilon_i - \epsilon_m \geq 0$  for all adsorption sites. The average value over all values  $\epsilon_{im}$  is defined as  $\epsilon^*$ . Thus, smaller values of  $\epsilon^*$  indicate that the adsorption energies of all sites do not differ greatly and that they are close to  $\epsilon_m$ . Under these conditions the adsorbent's surface is nearly homogeneous with respect to the adsorption energies of all sites. High values of  $\epsilon^*$  indicate the presence of sites with a greater distribution of adsorption energies compared to  $\epsilon_m$ .

Analysis of the calculated values of  $\epsilon^*$  summarized in Table I indicate that the heterogeneity of the modified carbons decrease in the order: AS-BA > AS-DNBA > AS-PMBA > AS-PNBA. Based on the above arguments, the minimum adsorption energy is mainly due to the benzene-ligand interaction; whereas the primary groups on the (unmodified) carbon surface aromatic sheets are main sources of surface heterogeneity. If these arguments are true, then the modified carbons with the smallest concentrations of bonded ligands should be more heterogeneous (higher values of  $\epsilon^*$ ) than those with the higher concentrations of the bonded ligands. As reported elsewhere chemical cleavage, extraction and high-performance liquid chromatographic analyses have shown that the ligand concentration on the modified carbons were<sup>13</sup>:  $2.1 \pm 0.8$  molecules/1000Å<sup>2</sup> for AS-BA,  $2.7 \pm 0.3$  molecules/1000Å<sup>2</sup> for AS-DNBA,  $3.3 \pm 0.4$  molecules/1000Å<sup>2</sup> for AS-PMBA and  $5.3 \pm 0.3$  molecules/1000Å<sup>2</sup> for AS-PNBA. A comparison of this order coincides with that obtained for the values of  $\epsilon^*$ . The smallest value of  $\epsilon^*$  was obtained for the AS-PNBA sample, which contained a highest concentration of the bonded ligands in comparison to the modified adsorbent indicating that it was less heterogeneous than other materials. The AS-BA and AS-DNBA modified carbons were more heterogeneous than the AS-PMBA and AS-PNBA carbons.

The sequence of the  $\ln V_{s,t}$  vs.  $1/T$  plots shown in Fig. 5 is determined by the slope and expression  $\ln(\alpha c_{s,t}^0)$ , which depends on the entropy parameter  $\alpha$ , and on the maximum solute concentration  $c_{s,t}^0$  of benzene on the modified carbon surface. It is difficult to estimate, how these quantities contribute to the value of  $\ln(\alpha c_{s,t}^0)$ . Because the bonded ligands have a complex chemical structure, the entropy effects arising from the different solute-ligand structures may be significant. Further theoretical and experimental studies are needed to provide a clear interpretation of the entropy effects in these complex chromatographic systems.

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