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International Science Publishers

Acid-Base Interactions: Relevance to Adhesion Science and Technology *Volume 2*

Editor: K.L. Mittal

Utrecht • Boston • Tokyo, 2000

Determination of the acid-base properties of solid surfaces using Inverse Gas Chromatography: Advantages and limitations

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Abstract—Inverse Gas Chromatography, at infinite dilution conditions (IGC-ID), is a convenient method for the examination of the surface properties of a solid. A comparison of apolar (n-alkanes) and polar probe adsorption behaviors leads to an estimation of the specific (polar, acid-base) interaction capacity of the solid surface. By knowing the acid-base characteristics of the probes, one may, in principle, assess the acid-base properties of the solid surface itself. The different approaches proposed in the literature are reviewed and discussed. The necessary choice of an (empirical) acid-base scale is of importance and will also be examined. Furthermore, the probe-surface interaction depends on steric factors. Recently, we proposed a procedure to take this parameter into account. However, the limitations of the IGC-ID method for the determination of the acid-base properties of a solid surface are essentially related to the unavoidable surface heterogeneity of any solid surface. Indeed, the IGC-ID fundamental equation assumes that the solid surface is quite homogeneous. In fact, this condition is scarcely fulfilled because of the existence of surface structural defects, variation in the nature and topology of surface groups, etc... As a consequence, the sites having the highest interaction potential will principally contribute to the retention time of the probe in the chromatographic column leading to acid-base parameters that are not representative of the whole surface of the solid.

Keywords: Inverse Gas Chromatography; morphology indexes; acid-base interactions; surface heterogeneity.

1. INTRODUCTION

Inverse Gas Chromatography at Infinite Dilution Conditions (IGC-ID) is a convenient method for the examination of the surface properties of a solid. But, as in the other methods based on wettability measurements (contact angle or liquid wicking measurements), the estimation of the specific (polar, acid-base) interaction capacity of the solid surface is obtained by a comparison of the apolar (n-alkanes) and polar probes adsorption behaviors.

Then, the first problem encountered is to estimate quantitatively the respective contributions of the non-specific forces and of the acid-base interactions, because when a polar molecule interacts with a solid surface, the non-specific forces related to

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the London forces and the specific ones, mainly due to acid-base interactions, take place simultaneously.

In the case of IGC-ID, for the estimation of the contribution of the specific component (ΔG_a^{sp}) to the free energy of adsorption, it was proposed to subtract from the global free energy of adsorption of the polar probe, the free energy of adsorption of a hypothetical alkane having the same molecular descriptor value. The earliest molecular descriptor used was the logarithm of the vapor pressure of the probe [1]. Later on, other molecular descriptors were suggested. Their validity will be discussed later. Finally, starting from the ΔG_a^{sp} values and calling on semi-empirical scales describing the acid-base properties of the probes, it is now possible to assess the acid-base properties of the solid surface itself.

Then, an important question is: Will the IGC-ID technique provide the same information as do wettability methods for the assessment of the acid-base characteristics of a solid surface? The latter are based on the interaction between a liquid (a condensed medium) and the solid surface, but the former, IGC-ID, is based on the measurement of the level of interaction between an isolated gaseous molecule and the solid of interest. In other words, wettability measurements will lead to an average macroscopic information whereas IGC-ID will be sensitive to local microscopic variations of the surface structure, at a molecular scale. Thus, wettability measurements will be sensitive to macroscopic geometrical factors, such as surface roughness and/or surface porosity and tortuosity of the macroporous structure. Local variations of the physico-chemical structure of the solid such as mesopores, micropores and crevices and/or the chemical composition variation will influence the IGC-ID measurements. Therefore, we may predict that wettability methods and IGC-ID techniques may provide comparable information, but only on quite homogeneous surfaces.

Coming back to IGC-ID, we shall first show how a comparison of the adsorption behaviors of linear and bulky alkanes and polar probes permits to evidence the surface roughness and acid-base properties. Thereafter, we shall discuss how surface energetic heterogeneity will affect the specific interaction of a polar probe with a solid surface.

2. DETERMINATION OF THE ACID-BASE INTERACTION USING IGC-ID

2.1. Measurement of the Specific Component of the Free Energy of Adsorption of a Polar Probe

Specific interactions include all types of interactions except the London or dispersive interactions. They may correspond to polar, ionic, electrical, magnetic, metallic, acid-base interactions, etc... Among them, acid-base interactions play a determinant role [2]. Assuming that these two types of interactions are additive, it follows that:

$$\Delta G_a = \Delta G_a^d + \Delta G_a^{sp} \quad (1)$$

According to the fundamental equation (2) of IGC-ID, the net retention volume V_n , that is the volume of carrier gas which is necessary to push the probe molecule

through the chromatographic column containing the solid of interest, is directly related to the partition constant K of probe molecules, between the adsorbed state and the gas phase, and to the total adsorption area A of the solid contained in the chromatographic column:

$$V_n = K \cdot A \quad (2)$$

Then the global free energy of adsorption ΔG_a of a probe is related to V_n by the equation:

$$-\Delta G_a = RT \ln(V_n/C) \quad (3)$$

where C is a constant related to the chosen reference state for the adsorbed molecule.

As pointed out above, a comparison of the apolar (n-alkanes) and polar probe adsorption behaviors leads to the evaluation of the contribution of the specific interactions (ΔG_a^{sp}), by subtracting, from the global free energy variation ΔG_a , the contribution due to dispersive interactions. The latter is estimated from the "n-alkanes reference line" observed when plotting the global free energy of adsorption ΔG_a of n-alkanes versus a given molecular descriptor that could be, for example, the number of carbon atoms or the vapor pressure of the injected probes. The representative points of polar probes, that are more interactive with the polar surface, should be located above the so-called "alkane-line" and the contribution of specific interactions (ΔG_a^{sp}) is then given by the departure of the representative point of the polar probe from this "reference alkane line" as shown in Figure 1.

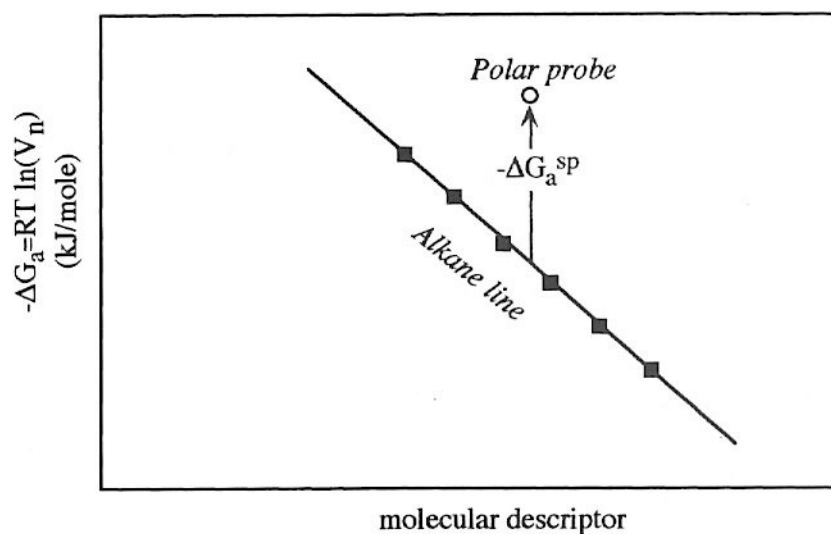


Figure 1. Principle of the determination of the specific component, ΔG_a^{sp} of the free energy of adsorption.

It is obvious that the choice of the molecular descriptor may influence notably the value of the measured ΔG_a^{sp} .

Mukhopadhyay and Schreiber [3] and more recently, Brendlé and Papirer [4] paid a special attention to the choice of the molecular descriptor, reviewing the different proposals made in the literature, namely:

- $\log(P_0)$, the logarithm of the vapor pressure [1],
- $a(\gamma^d)^{1/2}$, the product of the molecular area a by the square root of the dispersive component of the surface tension of the probe γ^d , taken in a liquid state [5],
- T_b , the boiling point [6],
- $\alpha_o(h\nu)^{1/2}$, the product of the polarisability α_o of the probe and the square root of its electronic frequency $\nu \cdot h$, where h is the Planck constant [7].
- X_t , a topological index [4] that takes into account both the geometry and the local electronic density due to the presence of heteroatoms, such as chlorine, oxygen or nitrogen atoms, in the polar probe structure.

The first descriptor was the earliest of the five and was proposed by Saint-Flour and Papirer [1] and remains up to now the most popular. The choice of this parameter was made considering that the logarithm of the vapor pressure which is closely related to the evaporation enthalpies (ΔH_v) was representative of the capacity of interactions of two identical molecules. This molecular descriptor presents several advantages since P_0 values are given in the literature or are computable even at relatively high measurement temperatures as long as these stay below the critical temperature of the probe. Yet, problems do appear with certain solids, possessing a high surface energy, since the representative points of some polar probes fall beneath the alkane-line. Chehimi and Pigois-Landureau [8] explained this observation in terms of the self-association of given polar probes and, moreover, they proposed to use the enthalpy of evaporation, ΔH_v , instead of $\log(P_0)$, correcting it by taking into account the contribution of the dispersive interactions to ΔH_v . Of course, ΔH_v and T_b are closely related physical parameters.

Later on, Schultz *et al.* [5] proposed to use the quantity $a(\gamma^d)^{1/2}$ as a molecular descriptor where a is the cross-sectional area of the adsorbed probe and γ^d the dispersive component of the surface tension of the probe, starting from equations established by Fowkes [9].

This procedure solved apparently some of the problems encountered using the earlier method. The limitations are due, in part, to the fact that the molecular area “ a ” is not exactly known and varies both with the nature of the solid [8], and the temperature and surface coverage. Furthermore, γ^d values are not always available from the literature at the temperature used for the IGC measurements. Both limitations are not recognized in the Schultz approach.

Finally, all preceding molecular descriptors suffer from the same weakness: they all are based on parameters that are characteristic of interactions between identical molecules in the liquid phase, whereas ΔG_a is related to the interaction between an isolated molecule and a solid surface having generally a very different chemical nature.

This observation instigated some authors to propose new molecular descriptors that are related to the molecular structure of the probe and not solely to the intermolecular interactions that take place between them in the liquid phase.

The first attempt was made by Dong *et al.* [10] and refined by Donnet *et al.* [7], who, starting from the equations describing the van der Waals interaction energy between two partners, proposed to adopt the product $\alpha_o(h\nu)^{1/2}$ as the molecular descriptor. The main difficulty encountered by these authors was due to the fact that polarizability data, measured at low frequency, are rather scarce in the literature, whereas those computed from refractive indexes according to the Debye relation are rough approximations.

Finally, Brendlé and Papirer [4] suggested that topology indexes, such as the Wiener ones [11, 12], which were extensively and successfully employed for the prediction of physicochemical molecular properties, such as boiling points, surface tensions and later for the understanding of the action of drugs [13] or crystal growth process modeling [14], could be used instead of the preceding molecular descriptors. They applied these topology indexes with success, at first, for describing the adsorption of branched alkanes used for testing, on a molecular scale, the surface roughness of the adsorbents (Size Exclusion IGC [15]). Then, calling on the method of Barysz *et al.* [16] that allows an easy extension of the Wiener indexes to polar probes, they proposed new topology indexes for the evaluation of a solid surface specific interaction potential.

For the sake of comparison, the variations of $RT \ln(V_n)$ of apolar and polar probes, measured at 110°C on a smooth fumed silica (Aerosil A130 from Degussa), with the four different molecular descriptors are shown in Figures 2 and 3.

Figures 3a and 3b look very similar. Actually, when plotting X_t versus $\alpha_o(h\nu)^{1/2}$, one obtains a quite linear correlation which is illustrated in Figure 4.

The main advantage of the X_t parameter is that it may be easily computed for each probe of interest, without any physical measurement requirement. The main molecular descriptors used for the IGC determination of the specific interactions are collected in Table 1.

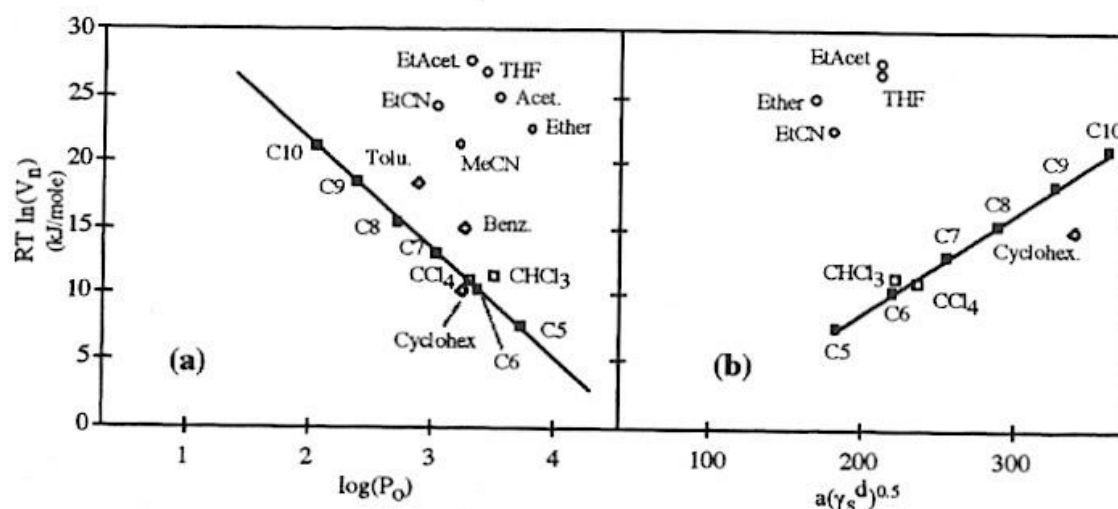


Figure 2. Variation of $RT \ln(V_n)$ of apolar and polar probes, measured at 110°C on a fumed silica (Aerosil A130 from Degussa), with $\log(P_0)$ and $a(\gamma_s^d)^{0.5}$, taken as molecular descriptors.

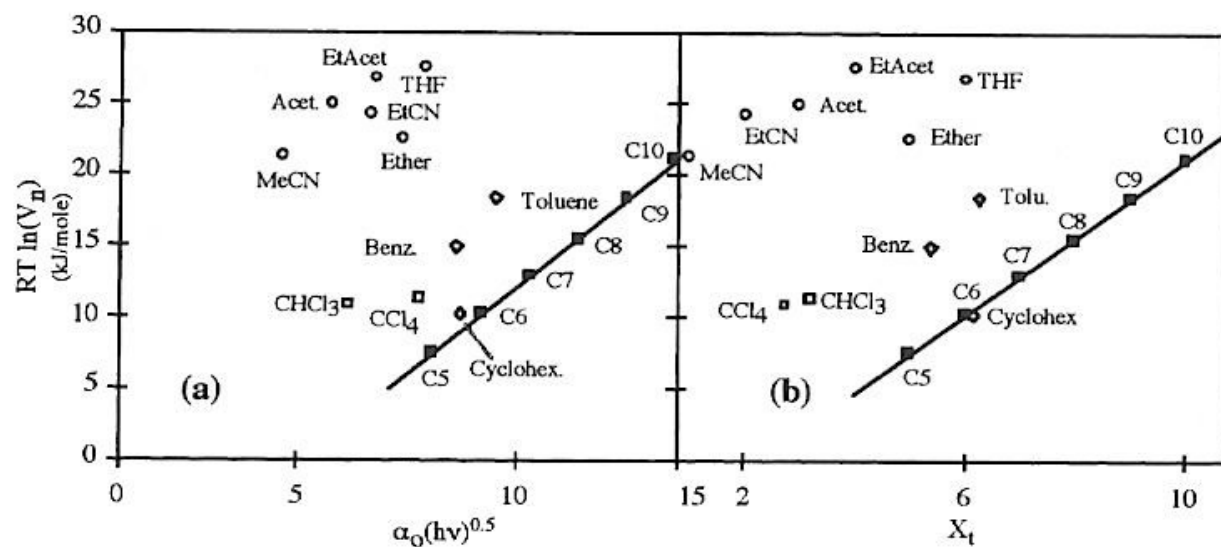


Figure 3. Variation of $RT \ln(V_n)$ of apolar and polar probes, measured at 110°C on a fumed silica (Aerosil A130 from Degussa), with $\alpha_o(h\nu)^{0.5}$ and X_t , taken as molecular descriptors.

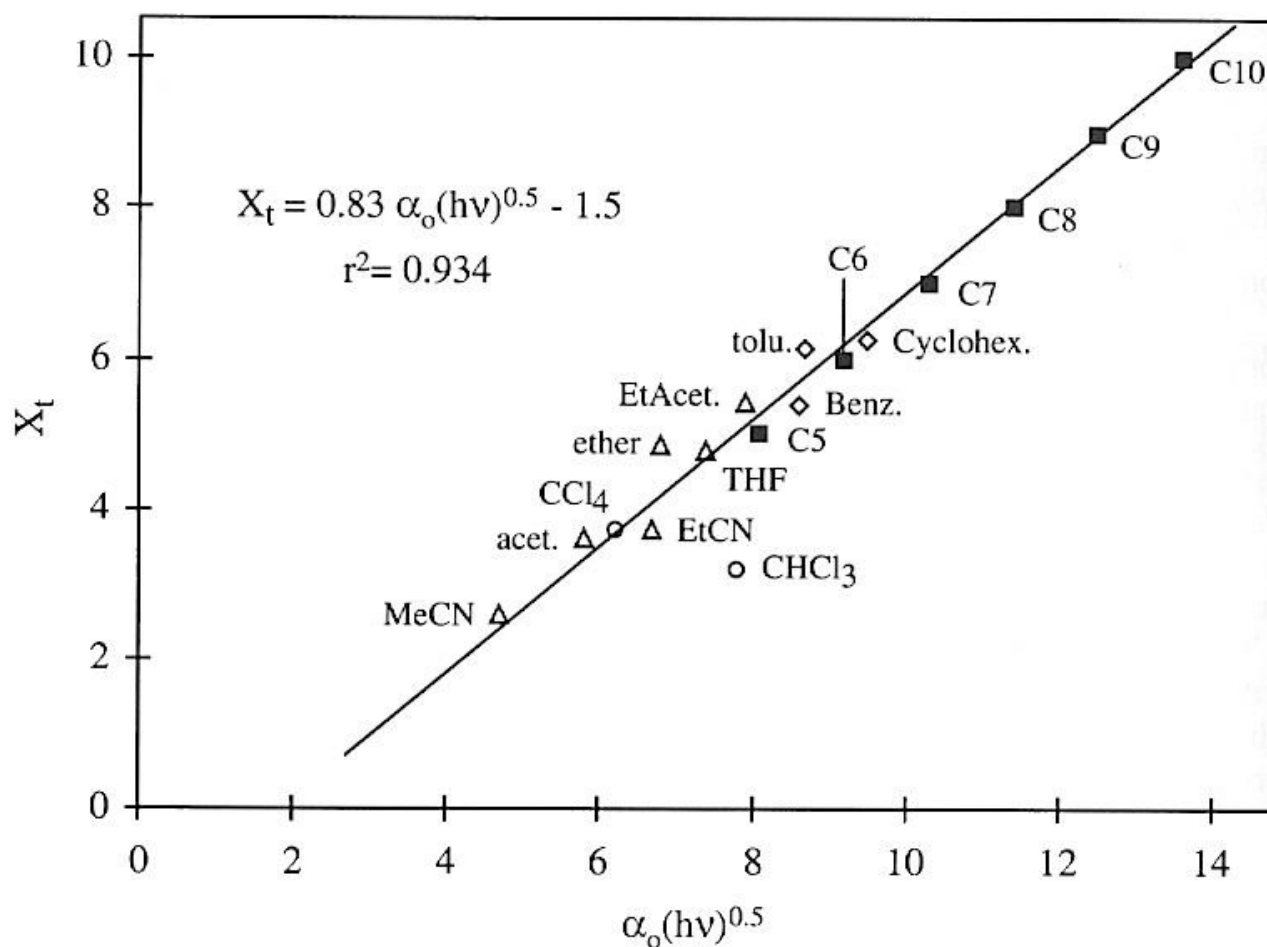


Figure 4. Variation of the topological index X_t with polarisability index $\alpha_o(h\nu)^{0.5}$.

Table 1.

Antoine's law parameters [1], indexes of surface tension [5], indexes of polarisability [7] and topology indexes [4] of some common IGC probes used for testing the acid-base properties of a solid surface

Probes	Designation*	A	B	C	$a(\gamma_s^d)^{0.5}$	$\alpha_0(h\nu)^{0.5}$ $\times 10^{49}$	X_t
Pentane	C5	6.8522	1064.6	232.00	185	8.1	5.00
Hexane	C6	6.8778	1171.5	224.34	221	9.2	6.00
Heptane	C7	6.9024	1268.1	216.90	257	10.3	7.00
Octane	C8	6.9238	1355.1	209.52	290	11.4	8.00
Nonane	C9	6.9351	1428.8	201.62	328	12.5	9.00
Decane	C10	6.9537	1501.3	194.48	363	13.6	10.00
Chloroform	CHCl ₃	6.9033	1163.0	227.40	224	7.8	3.21
Tetra-chloro-methane	CCl ₄	6.8941	1219.6	227.16	238	6.2	3.74
Cyclohexane	Cyclohex.	6.8450	1203.5	222.86	-	8.7	6.15
Benzene	Benz.	6.9057	1211.0	220.79	238	8.6	5.39
Toluene	Tolu.	6.9545	1344.8	219.48	-	9.5	6.26
Acetonitrile	MeCN	7.1226	1315.2	230.00	-	4.7	2.61
Propionitrile	EtCN	7.1522	1398.2	230.00	-	6.7	3.71
Acetone	Acet.	6.9033	1163.0	227.40	171	5.8	3.61
Ethyl Acetate	EtAcet	6.8941	1219.6	227.16	213	7.9	5.43
Ether	Ether	6.9847	1090.6	231.20	182	7.4	4.77
Tetrahydrofuran	THF	6.7538	1146.4	230.00	213	6.8	4.85

* for figure captions.

A, B, C are the parameters of Antoine's law for the calculation of the saturated vapor pressure.

$a(\gamma_s^d)^{0.5}$ is the surface tension index.

$\alpha_0(h\nu)^{0.5} \cdot 10^{49}$ is the polarisability index.

X_t is the topology index.

2.2. Assessment of the Acid-base Properties of a Solid Surface

The quantitative evaluation of acid-base interaction parameters for solid surfaces is generally based on ΔH_a^{AB} , the enthalpy of specific interaction between two molecules A and B. The different approaches in use were recently reviewed by Mukhopadhyay and Schreiber [3]. Only the Gutmann approach will be briefly recalled in this paper.

Adopting the Gutmann terminology [17], the probes are categorized as acidic, basic or amphoteric molecules by their electron-acceptor and their electron-donor numbers AN and DN , respectively (Table 2). The specific enthalpy of adsorption values ΔH_a^{sp} are computed directly from specific free enthalpies of adsorption, measured at different temperatures, according to Eq. (4).

$$\Delta H_a^{sp} = -T^2 \partial(\Delta G_a^{sp}/T)/\partial T \quad (4)$$

Following an extension of the Gutmann equation, which allows the calculation of the interaction enthalpy between a "pure" acid and a "pure" base, the specific interaction enthalpy (ΔH_a^{sp}) between an amphoteric (having both acid and base interactions capacities) probe, characterized by both AN and DN , and an amphoteric solid surface characterized by K_A and K_D (Acceptor and Donor numbers of the solid surface) is given by equation (5).

$$\Delta H_a^{sp} = AN \cdot K_D + DN \cdot K_A \quad (5)$$

K_A and K_D are graphically determined as shown in Figure 5 for a fumed silica surface (Aerosil A130 from Degussa) and its methylated derivative, by plotting $\Delta G_a^{sp}/AN$ (instead of ΔH_a^{sp} , since ΔG_a^{sp} is proportional to ΔH_a^{sp}) versus DN/AN .

From the slopes of the lines, the K_A values are obtained whereas the ordinates at the origin give K_D 's.

Table 2.

Acceptor [3] and Donor [4] numbers of some common polar probes

Probes	AN (%)	DN (kcal/mol)
Benzene	0.17	0.1
CCl ₄	0.7	0.0
Chloroform	5.4	0.0
Acetonitrile	4.7	14.1
Acetone	2.5	17.0
Ethyl Acetate	1.5	17.1
Ether	1.4	19.2
THF	0.5	20.0

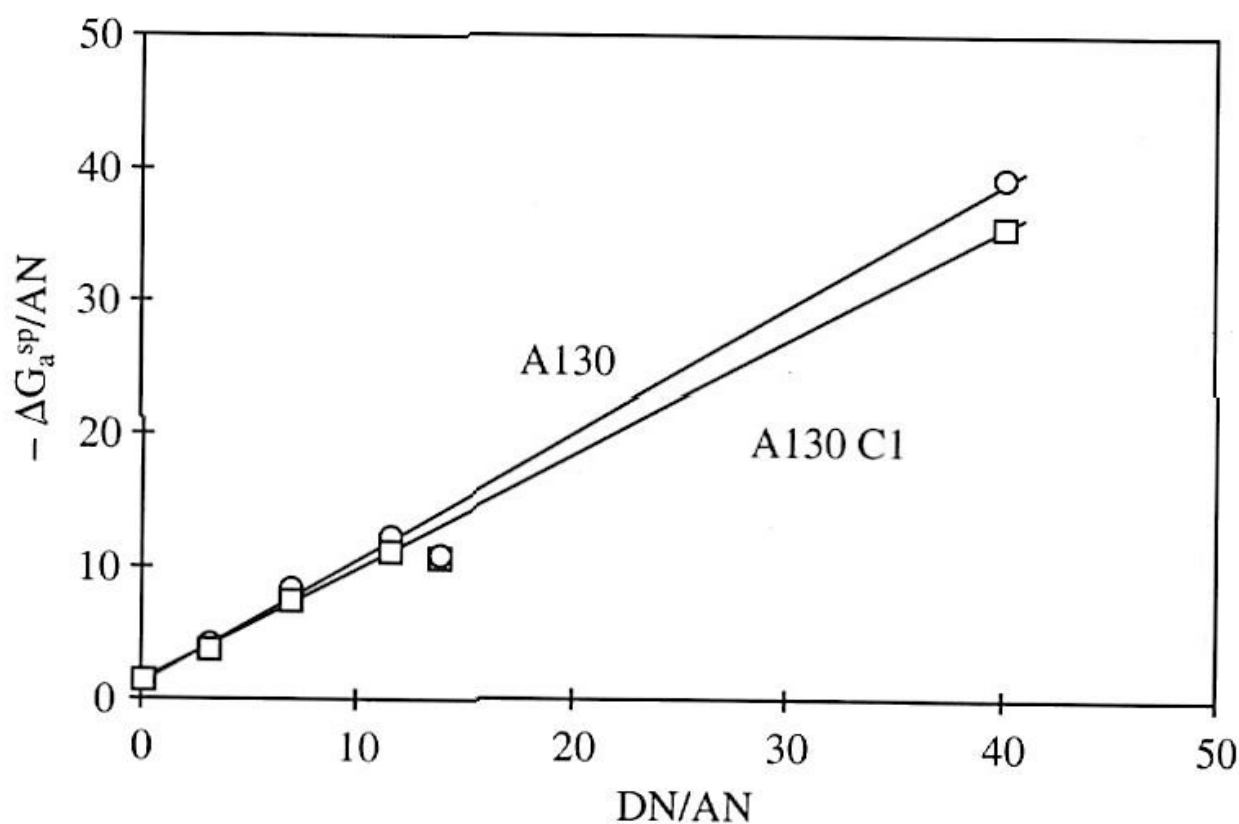


Figure 5. Determination of the K_A and K_D parameters on a fumed silica sample (Aerosil A130 - Degussa) and its methylated derivative (A130 Cl).

Table 3 gathers the main characteristics of these two analyzed samples.

As expected, the methylation of the fumed silica increases its electron-donor capacity which is mainly related to the presence of siloxane bridges on the silica surface, whereas the disappearance of silanol groups, due to the esterification of the most acidic isolated silanol groups, leads to a lower electron acceptor capacity.

Table 3.

Main characteristics of a fumed silica sample (A130) and its methylated derivative (A130 C1) and their respective acceptor K_A and donor K_D parameters measured at 110°C, using IGC-ID technique

	A130	A130 C1
Specific surface area (m ² /g)	130	130
OCH ₃ /nm ²	0	3.4
K_A	0.94	0.85
K_D	1.21	1.29
correlation coefficient	0.989	0.994

It would be interesting to go further in this direction so as to reach a more quantitative description of the acid-base properties of solid surfaces, but this would require a knowledge of the number of surface groups, per unit surface area, which interact with the probe: a quantity that is not easy to evaluate from the sole IGC measurements.

On an energetically homogeneous surface, the number of sites visited by the molecular probe depends on both the number of these sites n_s and on their energies of interaction ϵ_s . The experimentally measured retention time, t_r , may be considered as the product of local residence time, τ_s , and the total number of sites visited n_s Eq. (6) [19], the two variables which cannot be separately evaluated:

$$t_r = n_s \cdot \tau_s \quad \text{with} \quad \tau_s = \tau_0 \exp(\epsilon_s/RT) \quad (6)$$

where τ_0 is between 10^{-12} to 10^{-13} sec.

On a heterogeneous surface, the situation becomes much more complex and the influence of the surface energetic heterogeneity will be discussed more extensively later on.

The second reason that renders difficult a quantitative determination of acid-base characteristics of solid surfaces using the reported method stems from the fact that the semi-empirical acid-base scales of solutes were established considering the interactions between small organic molecules in solution. In a solvent, the two interacting molecules are free to adopt the best relative orientation leading to the highest level of interaction. This would certainly not be the case on a solid surface on which defects, steps, pores or crevices hinder the mobile probe molecule to adopt its optimal orientation, causing a decrease of the energy of interaction and this effect will also be dependent on the stereochemistry of the probe molecule itself.

Keeping in mind that the ΔG_a^{sp} determination is based on a comparison of the adsorption behaviors of n-alkanes and polar probes, it becomes evident that, if the size exclusion effects due, for instance, to given surface defects vary with the probe

stereochemistry, erroneous or apparent ΔG_a^{sp} will be obtained. The influence of the geometrical surface heterogeneity on the specific interactions will be discussed now.

3. LIMITATIONS OF IGC-ID

3.1. Influence of the Surface Morphology on the Specific Interaction Capacity

According to equation (2), a comparison of the retention properties of polar and non-polar probes assumes that both types of molecules should have access to the same area of adsorption; in other words, no size exclusion effects occur during the chromatographic process.

Papirer and Balard [20, 21] showed that such assumption of surface flatness could not be accepted for solids having a lamellar structure such as crystalline silicas or talc. If, for instance, partial insertion of alkanes occurs in slot like pores, on the lateral surface of the crystal, generated by stacking defects. This insertion will lead to a very efficient adsorption process of linear alkanes. From this insertion phenomenon, non-realistic high values of the dispersive component γ_s^d of the surface energy will be calculated for those materials. Then, negative I_{SP} values are also observed in that case, especially for bulky polar molecules such as chloroform or α - ω dienes that cannot access the same alkane adsorption sites [22].

Coming back to equation (2), a morphology index I_m was defined as the ratio of the true adsorption areas according to equation (7).

$$I_m = \frac{A_B}{A_L} = \frac{K_L}{K_B} \frac{V_N^B}{V_N^L} \quad (7)$$

where A_L and A_B are the areas of adsorption accessible, respectively, to linear and to the branched alkane probes and K_L and K_B their corresponding partition constants.

This takes into account the accessibility of the solid surface on the one hand and the shape or morphology of the molecular probe on the other hand. In this equation, the main problem encountered is the evaluation of the K_L/K_B ratio which obviously depends on the stereochemical structure of the branched alkane. In a first attempt, we proposed to determine this ratio for different branched alkane probes on a reference solid, a fumed silica sample (Aerosil A130). This silica may indeed be used as a model surface since independent methods such as volumetric gas adsorption, SAXS [23] and chemical approaches coupled with IGC [24] or NMR [25] had shown that its surface was smooth at the molecular level. The morphology index (I_m) we defined earlier [20] was then based on a simple comparison of the retention times of linear and branched alkane isomers on this pyrogenic silica and on the silica under investigation:

$$I_m = 100 \times \frac{V_N^B}{V_N^L} \frac{V_{Nref}^L}{V_{Nref}^B} \quad (8)$$

In this expression, V_N^L and V_N^B are, respectively, the net retention volumes of linear and branched alkanes, having the same number of C atoms, measured on the studied silica sample whereas $V_{N\text{ref}}^L$ and $V_{N\text{ref}}^B$ are the corresponding values for the reference pyrogenic silica.

A major difficulty when applying this method stems from the necessity of resorting to a reference solid surface having a different chemical structure than the solid of interest. Then, Brendlé and Papirer [15] proposed to assess this ratio K_B/K_L using new topology indexes X_t derived from Wiener's topology indexes [11]. Some X_t values [15] are reported in Table 4. Figure 6 illustrates this procedure for fumed silica (N20 from Wacker-Chemie GmbH).

Table 4.
Topology indexes X_t of some cyclic and branched alkane probes after [15]

Probes	Designation*	X_t
Cyclohexane	Cyclohex.	6.15
Cycloheptane	Cyclohept.	7.32
Cyclooctane	Cyclooct.	8.32
Methyl 2-butane	MeBut.	4.84
Methyl 2-pentane	MePent.	5.84
Methyl 2-hexane	MeHex.	6.84
Dimethyl 2,5-hexane	DMHex.	7.68
Trimethyl 2,2,4-pentane	TMPent.	7.40
Tetramethyl 2,2,3,3-butane	TeMBut.	7.09

* for figure captions

Figure 7 displays the same diagram established for H-Maggadiite, a crystalline silica having a lamellar structure.

It is seen that all cyclic and branched alkanes clearly lie below the "n-alkane line", a phenomenon due to the size exclusion effects leading to a strong decrease of the free energy of adsorption compared to the reference n-alkanes. The decrease in free energy, $-\Delta G_a^M$, equal to the departure of the representative point of the bulky alkane from the reference n-alkane straight line as depicted in Figure 7, corresponds to the contribution of the morphological factor to the loss of the interaction energy for a cyclic or a branched alkane probe.

$I_m(X_t)$, is then given by:

$$I_m(X_t) = \exp(-\Delta G_a^M/RT) \quad (9)$$

$I_m(X_t)$ was systematically measured on lamellar solids such as clay minerals [23], talc or muscovite [22] samples.

The $I_m(X_t)$ values measured on various silica samples, using different branched or cyclic alkanes, are listed in Table 5.

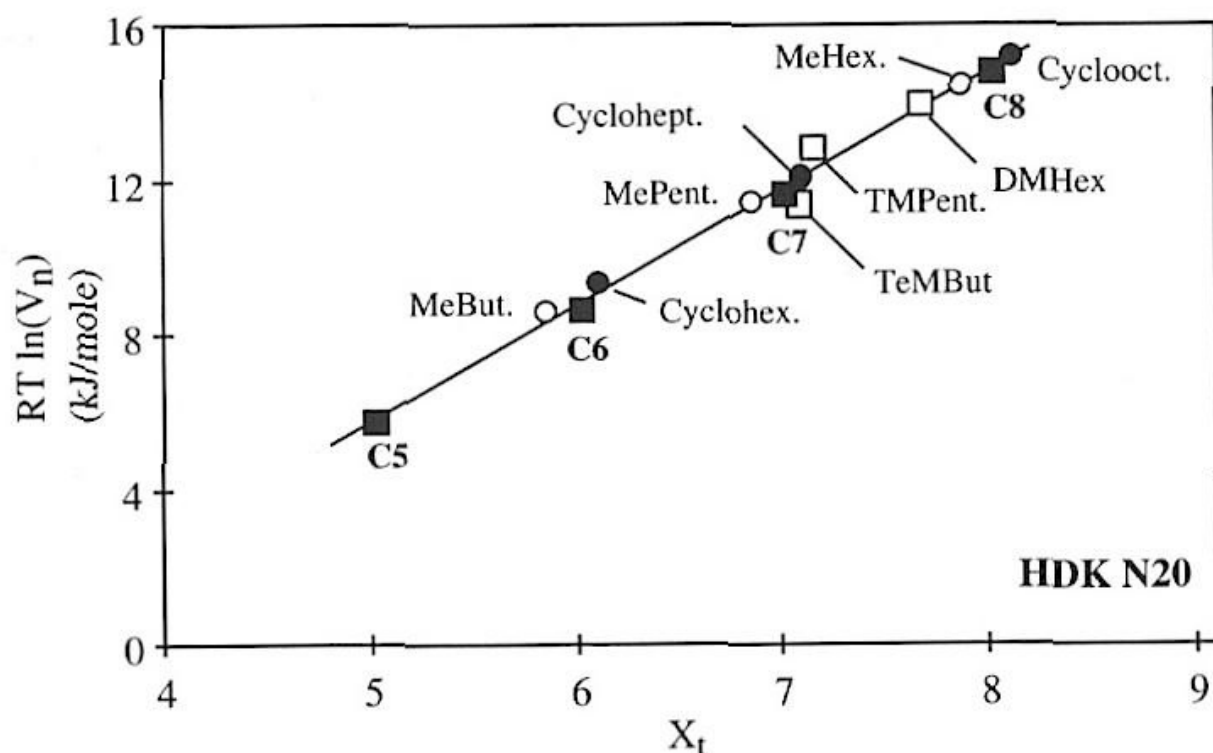


Figure 6. Variation of $RT \ln(V_n)$ with the topological index, X_t , of linear, cyclic and branched alkane probes for a fumed silica: HDK N20 from Wacker-Chemie GmbH.

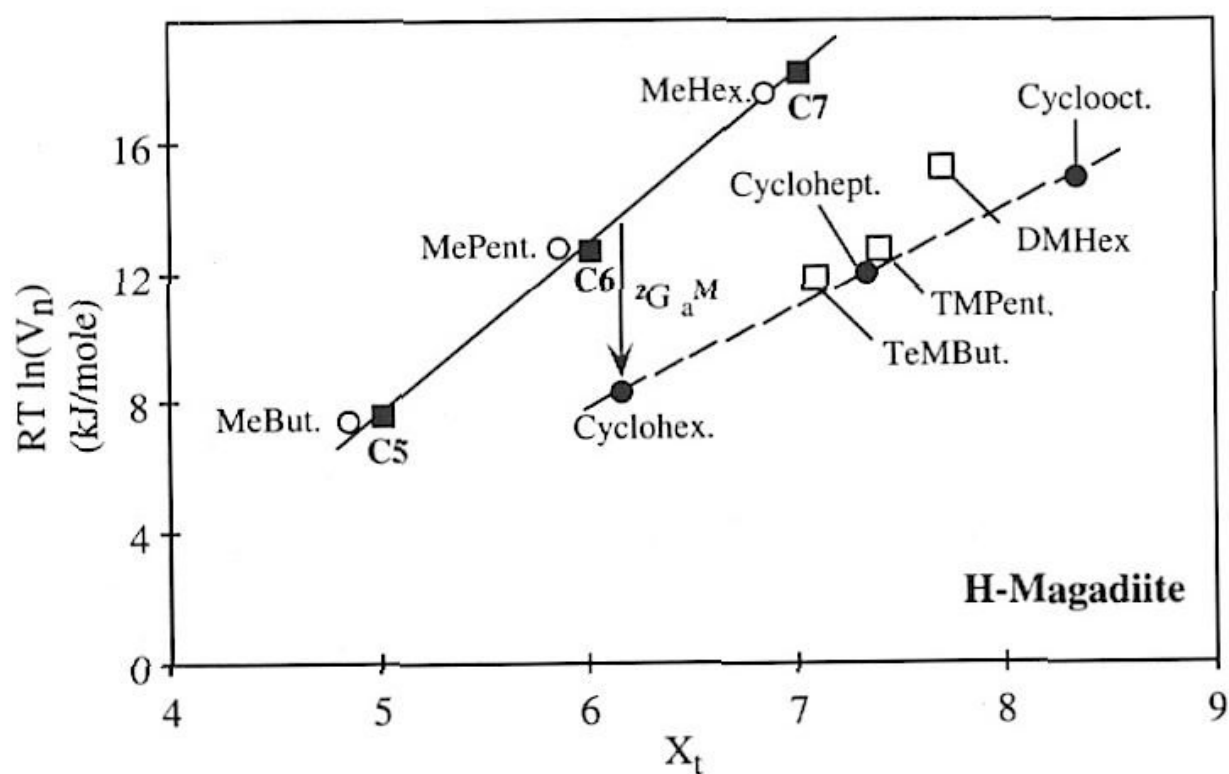


Figure 7. Variation of $RT \ln(V_n)$ with the topological index X_t of linear, cyclic and branched alkane probes for a crystalline silica: H-magadiite.

Table 5.

Decrease of the free energy of adsorption ΔG_a^M and morphology index I_m for cyclohexane and some branched alkanes measured on a fumed silica A130 (Degussa), two talc samples (Talc de Luzenac Europe), two clays: illite and kaolinite, and a crystalline silica: H-magadiite

	CycloHex		DMHex		TMPent		TMBut	
	ΔG_a^M (kJ/mole)	$I_m(X_t)$	ΔG_a^M (kJ/mole)	$I_m(X_t)$	ΔG_a^M (kJ/mole)	$I_m(X_t)$	ΔG_a^M (kJ/mole)	$I_m(X_t)$
Solids								
A130	-0.2	0.95	0.3	0.91	-0.3	1.10	-0.5	1.11
Talc 00	-	-	2.0	0.52	3.5	0.32	2.8	0.41
Talc sup	-	-	2.2	0.52	3.9	0.31	3.4	0.35
Illite Vosges	-	-	41.0	0.65	3.5	0.34	3.0	0.41
H-Magadiite	-5.47	0.19	-6.8	0.13	7.8	0.09	7.1	0.11

* Talc 00 and Talc sup are industrial references of Talc de Luzenac Europe.

Bulky polar probes, such as chloroform, do not have access to the adsorption sites accessible to linear alkanes. The decrement $-\Delta G_a^M$ will subtract from the increment, related to the specific interaction $-\Delta G_a^{sp}$, leading thus to an apparent lower global parameter of interaction I_{sp} . If the $-\Delta G_a^M$ exceeds $-\Delta G_a^{sp}$, we may observe a negative I_{sp} , having no physical meaning. Therefore, each time when exclusion effects are observed, one has to keep in mind that only apparent I_{sp} values are measured.

Finally, the last factor that can affect strongly the value of I_{sp} is the surface energetic heterogeneity.

3.2. Influence of the Surface Energetic Heterogeneity on the Specific Interaction Capacity

The IGC fundamental equation (2) assumes that the value of the partition constant K does not vary whatever the adsorption site, in other words the studied solid surface is assumed to be homogeneous.

In fact, this condition is scarcely fulfilled because atomic structures present on a solid surface are rigidly connected and this rigidity is responsible for the formation of surface defects like cracks, corners, steps and porous structures. Moreover, mineral and organic impurities often contaminate the solid surface. A consequence of the existence of surface heterogeneity is that the energy of interaction will vary depending on the chemical nature or local structure of the adsorption site visited by the probe. Hence, according to equation (6), the sites having the highest energies will principally contribute to the global retention time of the probe on the chromatographic support.

Moreover, due to the gradient of interaction energy originating from the surface heterogeneity, the adsorbed molecule will migrate on the surface towards the sites having the highest energy of interaction, sites that will act as potential wells, fixing the migrating molecule.

An indirect proof of this migration of the probe in the adsorbed state was given by the study of the surface properties, using IGC-ID, of fumed silica subjected to a controlled silylation (treatment with trimethylchlorosilane) process. It was observed that using both alkane probes (or poly(dimethylsiloxane) or PDMS oligomer probes) the

surface properties of the silylated silica samples changed suddenly when a coverage ratio of approximately 50% of the silica surface by the trimethylsilyl groups was reached. Such evolution is illustrated in Figure 8, in terms of the evolution of the increment of the free energy of adsorption per methylene group on fumed silicas (T30 silica from Wacker-Chemie GmbH) having an increasing trimethylsilyl coverage [26].

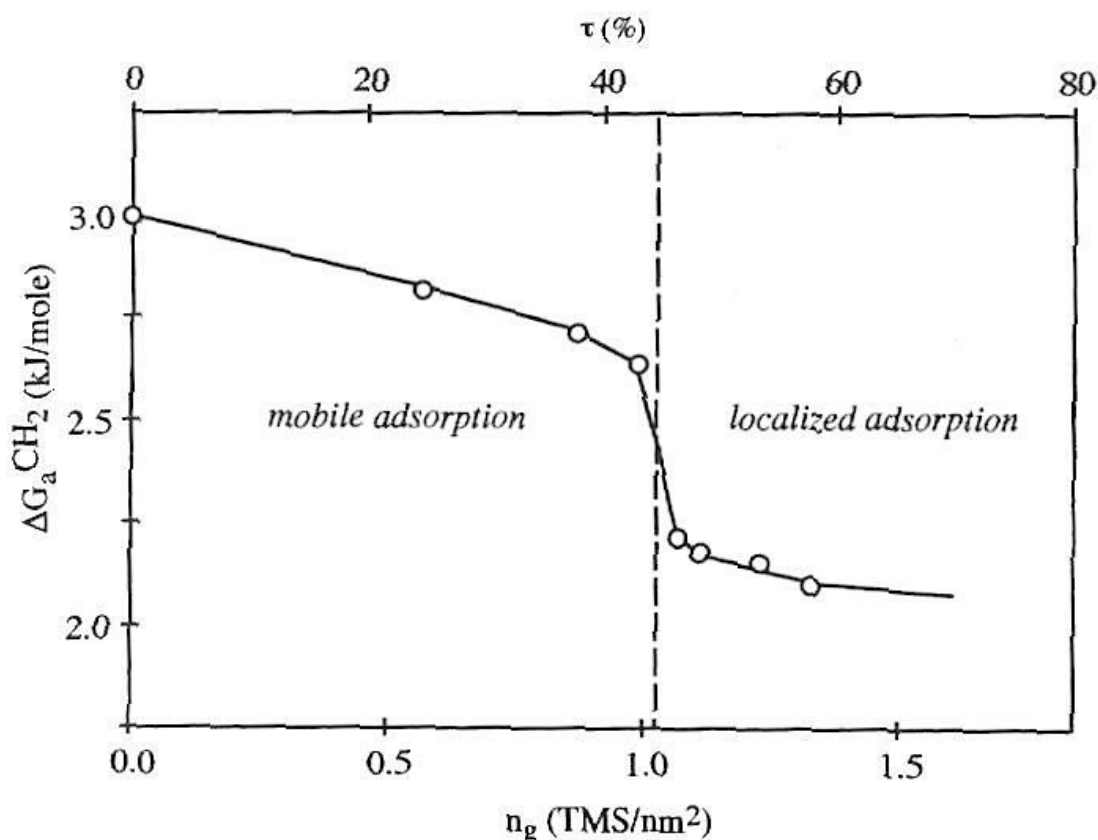


Figure 8. Variation of the increment of the free adsorption energy per methylene group $\Delta G_a^{CH_2}$ of n-alkanes with the trimethylsilyl (TMS) graft ratio n_g (in TMS/nm²) and the surface coverage ratio (in %), calculated for a TMS molecular area of 43 Å², for some silylated HDK T30 fumed silicas from Wacker-Chemie GmbH (measured at 150°C).

In a chromatographic process, a given molecule is submitted to a high number of sorption and desorption steps. If the motion of a molecule along the chromatographic column is mainly due to the carrier gas (usually He) flow, the probe molecule can also migrate on the solid surface itself. If the surface is energetically homogeneous, this phenomenon will have no influence on the measured retention time. On the contrary, on a heterogeneous surface, the sites having the highest energy of interaction will strongly retain the surface migrating molecule.

After a given time, the molecule will desorb and migrate in the gas phase. Therefore, the molecule visits only a very minor part of the solid surface. In other words, the probe will be most sensitive to the surface heterogeneity on a very short distance

that may be very roughly estimated to be a few molecular lengths, depending strongly, of course, on the temperature of measurement.

On a non-silylated initial silica, the adsorbed molecule can freely migrate between its site of adsorption and its site of desorption. In the case of a silylated silica sample, the trimethylsilyl grafts will act as pure geometrical barriers and will necessarily restrict the surface mobility of the probe. With increasing coverage ratios of the silica surface by the trimethylsilyl grafts, this limiting effect will increase. For coverage ratios higher than 50%, trimethylsilyl groups cover the majority of the surface and the residual accessible adsorption sites form only some "holes" in the continuous trimethylsilyl grafted layer. Consequently, the molecule can no longer migrate on the surface towards the more interactive sites and we do observe a sudden decrease of the increment in free energy of adsorption per methylene group.

Hence, the global retention time of the probe on a heterogeneous surface is a complex function of the energy of interaction of the sites present on the surface, their number and finally their capture radius because a strong interactive site can only capture a molecule that is adsorbed in its close environment. The global measured retention time t_r is then given by equation (10):

$$t_r = \sum (n_s, \epsilon_s, r_s) \quad (10)$$

where n_s is the number of sites having an energy of interaction ϵ_s and a capture radius r_s . All these parameters are presently unfortunately unknown.

Consequently, the thermodynamic values calculated from the retention time are not representative of the interaction capacity of the whole solid surface.

Moreover, the major contribution of the adsorption sites of the highest energy of interaction results in the fact that very often the most polar probes, like THF or diethylether, cannot be eluted from heterogeneous solids having, generally, a high specific surface area. Hence, only weak base probes such as aromatics or alkenes may be used in practice. Thus, it is impossible to determine meaningful acid-base properties of a solid.

A question is raised: is it possible to overcome partially these difficulties? The IGC at finite concentration conditions [27, 28] provides a possible but more time consuming way to assess the surface heterogeneity of a solid through the determination of the distribution functions of the adsorption energies of chosen solutes. Figure 9 displays such distribution functions established for octane, propanol-2 and pyridine on an industrial talc sample.

Obviously, the shapes of these distribution functions vary depending on the chemical nature of the probe: apolar like octane, acid like propanol-2 or a basic like pyridine. A challenge for the next years will be to extract from the adsorption energy distribution functions, K_A and K_D values as function of the solid surface coverage by the probes.

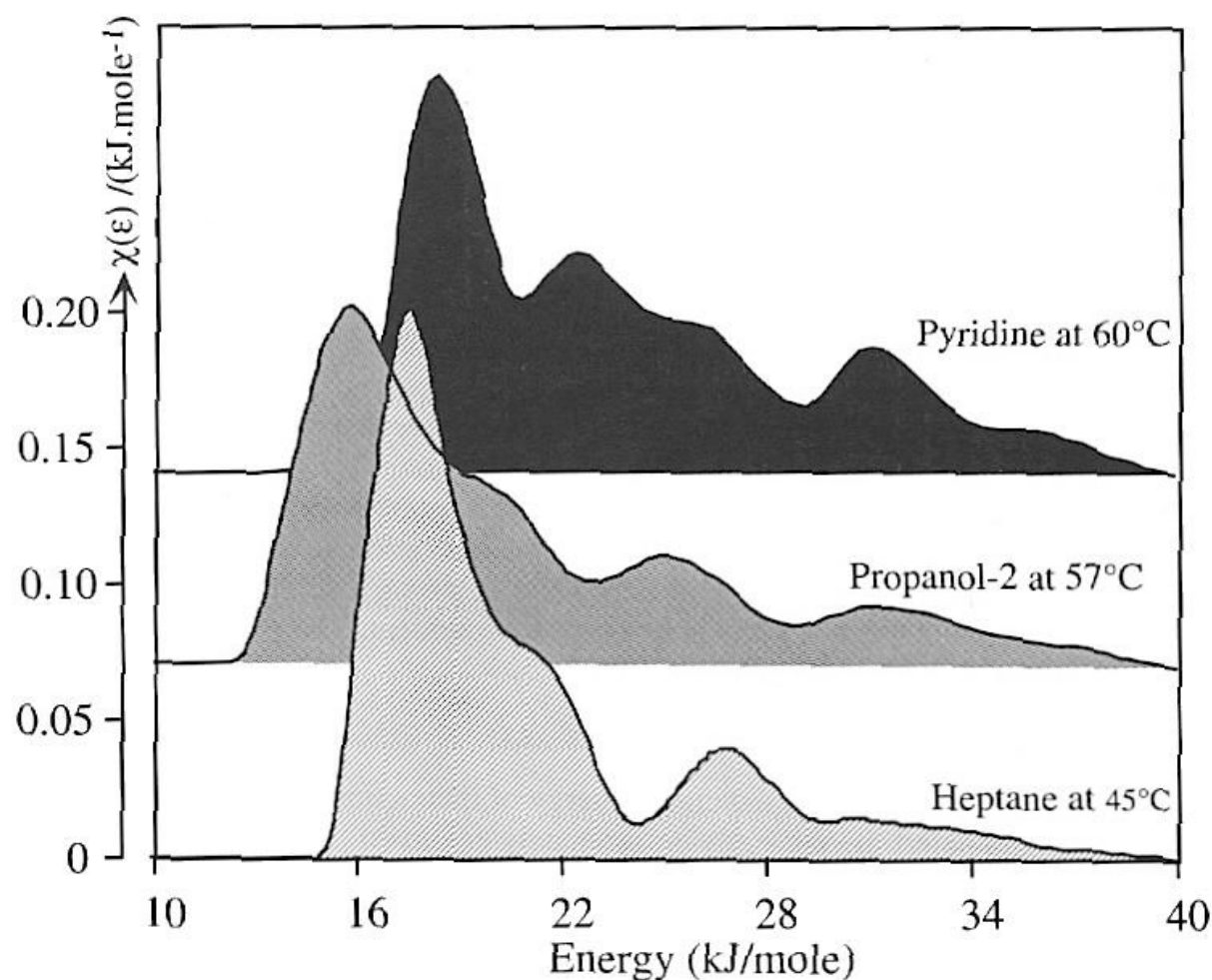


Figure 9. Distribution functions of the adsorption energies of n-heptane, propanol-2 and pyridine on a talc (Talc 00 from Luzenac Europe).

4. CONCLUSION

This paper emphasizes the importance of the choice of the molecular descriptor used for the separation of the contribution of the dispersive from the specific interactions when a polar molecule interacts with a polar solid surface. Molecular descriptors that are related to the probe/probe interactions in the liquid state have to be rejected because they will certainly be unable to take into account the interaction between an isolated molecule and a solid surface having generally a very different chemical nature.

On the contrary, polarisability index, which is only related to the probe chemical structure, will provide a good description of the dispersive interaction capacity of the IGC probe. Fortunately, although the literature data on molecular polarisability at low frequency are rather scarce, topological indexes, calculated from their molecular structures, are directly related to their polarisability indexes and can be advantageously used instead of polarisability indexes for the assessment of the specific adsorption free energies of polar probes.

By applying "classical approaches", based on a semi-empirical description of the acid-base properties of polar probes, the acid-base capacity of interaction of a solid can be estimated. However, this estimation will be valid only on quite smooth and homogeneous surfaces.

Moreover, the IGC method suffers also from some limitations. The first is related to the solid surface roughness. When this is not negligible, then the size exclusion effects will take place, which will influence the interaction capacity of the most bulky probes, in comparison to the reference linear alkanes, leading to undervalued I_{sp} .

On the contrary, surface heterogeneity may enhance I_{sp} , due to the dominant contribution, to the retention time of the probe, of the adsorption sites having the highest energy of interaction. For solids having a high specific surface area and a high surface heterogeneity such as carbon black or silicas, the main limitation of the IGC-ID method, for the assessment of the acid-base properties, is related to the fact that the interesting IGC polar probes are almost irreversibly adsorbed.

Nevertheless, the IGC-ID technique will possibly remain the most attractive and versatile method for determination of acid-base interactions on solids that are not too heterogeneous from both geometrical and energetic points of view.

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