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New approach to characterise physicochemical properties of solid substrates by inverse gas chromatography at infinite dilution III. Determination of the acid–base properties of some solid substrates (polymers, oxides and carbon fibres): a new model

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Abstract

In this paper, the inverse gas chromatography (IGC) technique was used to calculate the acid–base superficial characteristics of some solid substrates such as oxides, polymer and polymer adsorbed on oxide. The acid–base constants were calculated for many solids: Monogal, MgO, ZnO, SiO₂ and Al₂O₃, four different carbon fibres and polymers such as poly(methyl methacrylate) (PMMA) at various tacticities adsorbed on alumina or silica. The determination, by IGC, of the specific free enthalpy ΔG_a^{sp} of adsorption corresponding to the specific interactions of polar molecules with the solid, as a function of the temperature, allowed to obtain the specific enthalpy ΔH_a^{sp} and specific entropy ΔS_a^{sp} . Knowing ΔH_a^{sp} of the various polar molecules, we were able to determine the acidic constant K_A and basic constant K_D , the two constants characterizing solid substrates like PMMA, PMMA–SiO₂ or PMMA–Al₂O₃, using the following classical expression:

$$-\Delta H_a^{sp} = K_A DN + K_D AN$$

where DN and AN are respectively the electron donor and acceptor numbers of the solid substrates. This study showed an important effect of the tacticity on the acid–base properties. On the other hand, we proved that the previous relation was not correct in many cases and especially for some oxides (as MgO, ZnO and Monogal) and carbon fibres. We proposed a new relationship by adding a third parameter K reflecting the amphoteric character of the solid according to:

$$-\Delta H_a^{sp} = K_A DN + K_D AN - KDN \times AN.$$

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1. Introduction

The study of acid–base properties of oxide and hydroxide surfaces is of vital importance in physical chemistry, in particular in adhesion. Many methods

are proposed in the literature to understand and quantify the acid–base interactions at interfaces of such mineral oxides [1]. Acidity of a solid surface can usually be characterized by its point of zero charge (*PZC*), which corresponds to the pH at which the solid has no net surface charge [2]. *PZC* can be predicted by using Parks' equation [3,4] which is essentially a function of (Z/r), where Z is the formal charge of the cation and r is the sum of the cationic radius and the oxygen diameter (2.8 Å) [2]. This theory is basically related to the Brønsted acidity (see [1]). Recently, acid–base interactions at interfaces have been studied extensively in colloidal systems [5,6]. Fowkes and co-workers [7,8], in particular, have studied the adsorption of acidic and basic molecules from neutral solvents on inorganic powders such as iron, silicon and titanium oxides. They found that the calorimetric heats of adsorption are actually the heats of acid–base interactions, governed by Drago et al.'s equation [9], and that Drago et al.'s equation constants can be accurately determined for the surface sites of these inorganic solids. On the other hand, it is known [10–13] that when strong electron acceptor (Lewis acids) or donor (Lewis bases) entities are adsorbed on metal oxides, the corresponding radicals are formed as a result of electron transfer between the adsorbed molecules and the metal oxide surface. Such electron donor–acceptor interactions at interfaces become important for elucidating the adhesion forces at these interfaces [14]. It was Fowkes who first proposed in the field of adhesion to describe non-dispersive or specific interactions in terms of acid–base or electron donor–acceptor interactions [15,16]. Fowkes then considered these non-dispersive interactions to be identical to electron donor–acceptor or acid–base interactions.

Polar molecules used to determine the specific interactions with the solid substrates are characterized by their donor (DN) and acceptor (AN) numbers [17]. The concept of donor–acceptor interactions is an extension of the Lewis acid–base reactions, dealing with coordinate bonds which are formed by sharing a pair of electrons between donor and acceptor species.

Later, an empirical relationship was proposed [18] to characterize the solid with two constants: acidic constant K_A and base constant K_D :

$$-\Delta H^{sp} = (K_A DN + K_D AN) \quad (1)$$

where ΔH^{sp} is the specific enthalpy of adsorption deduced from the variation of the specific free enthalpy ΔG^{sp} as a function of the temperature ($\Delta G^{sp} = \Delta H^{sp} - T \Delta S^{sp}$). The knowledge of the ΔH^{sp} of various polar molecules allows us to determine the two constants K_A and K_D of the solid by plotting ($\Delta H^{sp}/AN$) as a function of (DN/AN), according to Eq. (1).

We will try in this paper to prove that Eq. (1) is, in general, not verified in the case of some metallic oxides. But Eq. (1) is accurate enough for many other solid substrates such as polymers and especially for poly(methyl methacrylate (PMMA) in the bulk phase or in adsorbed form.

Another more precise relationship is therefore proposed. A technique used to calculate specific enthalpies is inverse gas chromatography (IGC) at infinite dilution. Other information (*PZC* and dispersive interactions with some organic molecules) on these oxides was obtained in a previous study [19]. Previous results proved that MgO is more basic ($PZC = 11$) than the other oxides, whereas Monogal (an industrial oxide composed largely of ZnO) is the most acidic, in terms of the Brønsted acid–base concept.

We previously proved how inverse gas chromatography (IGC) can be used to determine some of the surface characteristics of various polymers or oxides, especially their surface energies and the transition temperatures of polymers like PMMA, where we generally detected three particular temperatures that can be affected by the tacticity of the polymer.

In this part, we also used IGC at infinite dilution [20] to determine the acid–base properties of PMMA, silica, alumina, and of PMMA–alumina and PMMA–silica systems, by varying the tacticity of the polymer and the recovery fraction of PMMA adsorbed on oxides.

Other solid substrates were also studied, such as Monogal, MgO, ZnO, and four different carbon fibres.

2. Methods and models

2.1. Principle

In this part, IGC at infinite dilution [20] was used

to study the acid–base properties of many solid substrates (polymers, oxides and polymers adsorbed on oxides).

Probes of known properties are injected in the column containing the solid. The retention times of these probes, measured at infinite dilution, allow us to determine the interactions between the organic molecules and the solid, if we suppose that there are no interactions between the probe molecules themselves. Measurements are carried out with a DELSI GC 121 FB Chromatograph equipped with a flame ionization detector of high sensitivity.

The net retention volume V_n was calculated from:

$$V_n = j D_c (t_R - t_0) \quad (2)$$

where t_R is the retention time of the probe, t_0 the zero retention reference time measured with a non adsorbing probe such as methane, D_c the corrected flow-rate and j a correction factor taking into account the compression of the gas [20]. D_c and j are respectively given by the following expressions:

$$D_c = j D_m \cdot \frac{T_c}{T_a} \cdot \frac{\eta(T_c)}{\eta(T_a)} \quad (3)$$

with

$$j = \frac{3}{2} \cdot \frac{\left(\frac{\Delta P + P_a}{P_a}\right)^2 - 1}{\left(\frac{\Delta P + P_a}{P_a}\right)^3 - 1} \quad (4)$$

where D_m is the measured flow-rate, T_c the column temperature, T_a the room temperature, $\eta(T)$ the viscosity gas, P_a the atmospheric pressure and ΔP the pressure variation.

The free energy of adsorption ΔG^0 of n -alkanes is given by:

$$\Delta G^0 = RT \ln V_n + C \quad (5)$$

where R is the ideal gas constant, T the absolute temperature and C a constant depending on the reference state of adsorption. In the case of n -alkanes, ΔG^0 is equal to the free energy of adsorption corresponding to dispersive interactions ΔG^d only.

The net retention volume will permit to obtain $RT \ln V_n$ and the free enthalpy of adsorption ΔG^0 of n -alkanes. In the case of n -alkanes, ΔG^0 is equal to

the free enthalpy of adsorption corresponding to dispersive interactions ΔG^d only. Studying the evolution of ΔG^d or of $RT \ln V_n$ versus $(1/T)$, we can obtain some interesting physico-chemical properties of polymers and especially, the second order transition temperatures (see Part II).

2.2. Study of specific interactions and acid–base constants

2.2.1. Determination of specific interactions

The specific interactions of the various solid substrates were determined by IGC at infinite dilution, using the principle detailed in Section 2.1. It is based on the determination of the net retention volume V_n of the probes (of known properties) injected in the column that contains the solid to be characterised. The free enthalpy ΔG^0 of adsorption of the probes on the solid can be obtained from the following relation:

$$-\Delta G^0 = RT \ln V_n + C \quad (6)$$

where R is the perfect gas constant, T the absolute temperature and C is a constant.

Papirer and co-workers [21–23] have obtained a straight line when plotting $RT \ln V_n$ against $\ln P_0$, where P_0 is the vapour pressure of the probes. For a homologous series of n -alkanes, they wrote:

$$RT \ln V_n = A \ln P_0 + B \quad (7)$$

where A and B are constants depending of the nature of the solid substrate.

When polar molecules are injected into the column, specific interactions are established between these probes and the solid surface and ΔG^0 is now given by:

$$\Delta G^0 = \Delta G^d + \Delta G^{sp} \quad (8)$$

where ΔG^{sp} refers to specific interactions and ΔG^d to the dispersive interactions.

The specific enthalpy ΔH^{sp} and entropy ΔS^{sp} of interaction between a polar molecule and a solid can be determined by using the method developed by Papirer and co-workers [21–23]. In Fig. 1, we give, as an experimental example, the variations of $RT \ln V_n$ as a function of $\ln P_0$ for different polar molecules interacting with PMMA adsorbed on alumina. Note

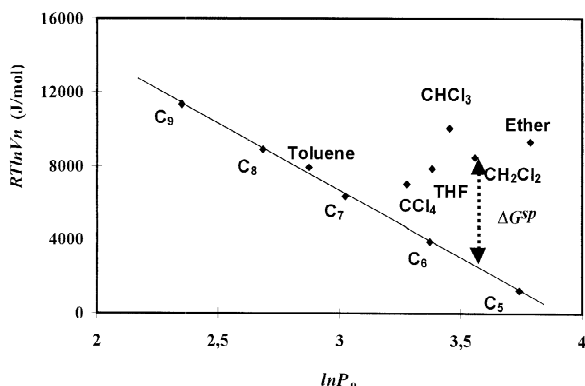


Fig. 1. Variation of $RT \ln V_n$ as a function of $\ln P_0$ for different polar molecules adsorbed on the atactic PMMA–alumina system.

the magnitude of ΔG^{sp} of CH_2Cl_2 adsorbed on the PMMA–alumina system at 25 °C.

Plotting ΔG^{sp} of the polar molecules as a function of the temperature, we can deduce the specific enthalpy (ΔH^{sp}) and the specific entropy (ΔS^{sp}) from:

$$\Delta G^{sp} = \Delta H^{sp} - T \Delta S^{sp} \tag{9}$$

or by dividing by T :

$$\Delta G^{sp}/T = \Delta H^{sp}/T - \Delta S^{sp} \tag{10}$$

We can also plot the variations of $(\Delta G^{sp}/T)$ as a function of $(1/T)$ for all polar molecules and then deduce ΔH^{sp} and the specific entropy ΔS^{sp} of different polar molecules adsorbed on the solid substrates. Fig. 2 gives some experimental curves

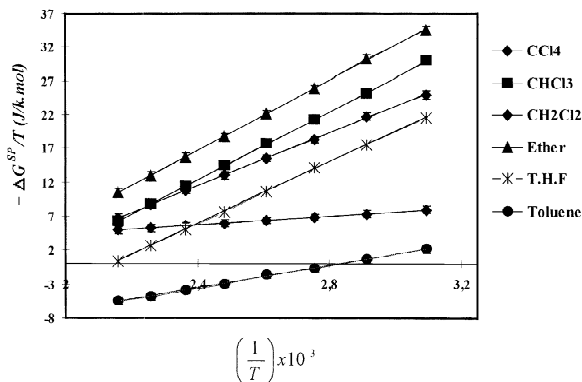


Fig. 2. Variations of $\Delta G^{sp}/T$ as a function of $1/T$ (T in K) for some polar molecules adsorbed on the atactic PMMA–alumina system.

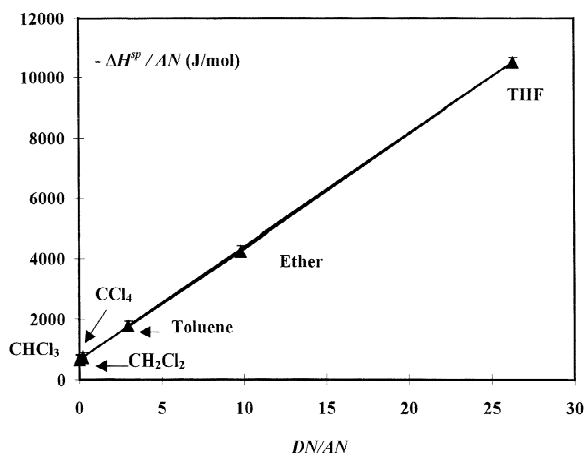


Fig. 3. Evolution of $-\Delta H^{sp}/AN$ as a function of DN/AN of some polar molecules adsorbed on the atactic PMMA–alumina system.

obtained in this study with atactic PMMA, showing the evolution of $(\Delta G^{sp}/T)$ as a function of $(1/T)$ for several polar molecules.

2.2.2. Determination of acid–base constants of a solid

To determine the specific interactions with the solid substrates, we used polar molecules that are characterised by their donor (DN) and acceptor (AN) numbers of electrons [17].

Deducing ΔH^{sp} of the various polar molecules from Eq. (9), we can determine the acidic constant K_A and basic constant K_D of the solid substrate, using the classical relationship given by Eq. (1) that can be also written as:

$$(-\Delta H^{sp}/AN) = K_A (DN/AN) + K_D \tag{11}$$

K_A and K_D can be obtained by plotting $(-\Delta H^{sp}/AN)$ as a function of (DN/AN) , according to Eq. (11).

We generally used Eq. (11) to deduce the acid–base constants for many solid substrates and especially for polymers. We present in Fig. 3 the results obtained in the case of the adsorption of atactic PMMA on alumina. The curve obtained is a straight line and Eq. (11) is verified in this case.

3. Materials and equipment

The chemical products used had the following characteristics:

α-Alumina, silica and PMMA: the details concerning these materials were given in Part II.

ZnO: powder of zinc oxide from Sigma–Aldrich (St. Quentin Fallavier, France) with high purity (>99%) exhibiting a specific area equal to 4 m²/g.

MgO: powder of magnesium oxide from Cerac-Neyco (Paris, France) with a 99.95% purity having a specific surface area equal to 2 m²/g.

Monogal: Monogal is an industrial product from Cerac-Neyco (Paris, France) that contains zinc oxide in majority, 0.3% of aluminium and 0.2% of free oxygen. Its specific surface area is about 0.16 m²/g.

Carbon fibres: four high strength polyacrylonitrile (PAN) based carbon fibres from Soficar (Pau, France) corresponding to different stages of manufacturing have been used in this study: the untreated fibre (UF); the untreated fibre having received a proprietary surface treatment through electrolytic oxidation, designated oxidised fibre (OF); the two oxidised fibres having received a supplementary sizing treatment: the first one is coated by an epoxy-polyester polymer denoted CF1 and the second is coated by an epoxy polymer denoted CF2. The diameter of the fibre is about 300 μm.

N.B. The PAN-based carbon fibres have various excellent properties:

- (i) Mechanical properties: lower density than metal, high tensile strength and tensile modulus, and good fatigue resistance, wear resistance and lubrication.
- (ii) Thermal properties: low linear expansion coefficient, good dimensional stability, high resistance to mechanical-property deterioration caused by heat, and low thermal conductivity at extremely low temperatures.
- (iii) Electric and electromagnetic properties: electric conductivity, ability to shield electromagnetic waves, and excellent X-ray penetrability.
- (iv) Chemical and physicochemical properties: good chemical stability and excellent resistance to acid, alkali, and various types of solvents.

Model organic molecules: we used some organic polar molecules such as toluene, ethanol, diethyl ether, ethyl acetate, acetone, tetrahydrofuran (THF), CCl₄, CHCl₃, CH₂Cl₂, CH₃CN and C₆H₆, which are characterized by their donor and acceptor numbers [17,24]. We also used *n*-alkanes (C₅H₁₂, C₆H₁₄, C₇H₁₆, C₈H₁₈, C₉H₂₀, C₁₀H₂₂, etc.) as non-polar

molecules. All organic molecules used in this study were purchased from Prolabo (Strasbourg, France).

We used in this study corrected acceptor number AN', given by Riddle and Fowkes [25] who subtracted the contribution of Van der Waals interactions (or dispersion forces). Donor number was normalised and used like a dimensionless number ND' [19] by using the following relationship:

$$ND' = 2.5 ND \text{ (kcal/mol)}$$

(1 cal=4.184 J). Table 1 gives donor and acceptor numbers of solvents used in this study.

Measurements of retention volumes of molecules were carried out with a DELSI GC 121 FB Chromatograph from Delsi Instruments (Suresnes, France) equipped with a flame ionization detector of high sensitivity.

In this part, we studied by IGC the following solid substrates in powder form: PMMA (at various tacticities), silica, alumina, ZnO, MgO and Monogal particles (about 1.5 g) having diameters between 100 and 200 μm, which were introduced in the column. Helium (He) was selected as carrier gas at a flow-rate of about 25 ml.min⁻¹. Before measurements, the polymer or oxide particles were conditioned in the column under a He flow during 12 h at 120 °C. IGC under infinite dilution conditions was used with minor amounts of gaseous solutes injected so as to approach near zero surface coverage, permitting to neglect lateral interactions between adsorbed molecules and the observation of symmetrical chromatographic peaks. IGC measurements at infinite dilution were performed by varying the temperature from 20 °C to 180 °C. The retention times obtained by this study allowed to obtain the net retention volume using Eq. (2).

The same procedure was used with four different

Table 1
Values of donor and acceptor numbers of various solvents

Solvent	DN'	AN'
CCl ₄	0	2.3
CHCl ₃	0	18.7
CH ₂ Cl ₂	3	13.5
THF	50	1.9
Toluene	9.75	3.3
Diethyl ether	48	4.9

Table 2
Values of acidic and basic constants of different PMMAs (atactic, isotactic and syndiotactic)

Solid substrate	K_A (kJ/mol)	K_D (kJ/mol)	K_D/K_A
Atactic PMMA	0.35 ± 0.06	1.31 ± 0.07	3.74 ± 0.09
Isotactic PMMA	0.42 ± 0.08	0.47 ± 0.06	1.12 ± 0.08
Syndiotactic PMMA	0.29 ± 0.06	0.76 ± 0.08	2.62 ± 0.09

carbon fibres and PMMA (at various tacticities) adsorbed on alumina or silica, by using the same experimental conditions.

4. Results

4.1. Acid–base constants of PMMAs, oxides and PMMA–oxides

The variation of the specific free enthalpy ΔG^{sp} was obtained by applying the IGC technique at infinite dilution and by using the method previously developed in paragraph 2.1. Using Eq. (4), we deduced ΔH^{sp} and ΔS^{sp} of the specific interaction between polar molecules and the solid substrate. By applying Eq. (7), we determined the acid K_A and base K_D constants of these solids. Using PMMA at

different tacticities, the results obtained showed an important effect of the tacticity on the acid–base properties of the polymer. We classified the various PMMAs by decreasing order of their basic character (Table 2):

atactic (a)PMMA > syndiotactic (syndio)PMMA
> isotactic (iso)PMMA

and by decreasing order of their basic character:

isotactic PMMA > atactic PMMA
> syndiotactic PMMA.

Our results showed that the acid and base character is extremely dependent on the tacticity of PMMA adsorbed on α -alumina or on silica. In Tables 3 and 4, we give the results obtained with PMMA at different tacticities and adsorbed on alumina or silica. Table 3 shows that the isotactic polymer strongly interacts with the alumina surface by its basic ester groups. This decreases the basicity of the PMMA–alumina system. In the case of syndiotactic PMMA, some basic groups do not interact with alumina and this confers to the covered surface a more pronounced basic character than for isotactic PMMA, but less pronounced than that of the atactic polymer.

The experimental results obtained with silica and

Table 3
Values of acidic and basic constants of the various PMMA adsorbed on α -Al₂O₃

Solid substrate	K_A (kJ/mol)	K_D (kJ/mol)	K_D/K_A
α -Alumina	0.67 ± 0.10	2.50 ± 0.40	3.7 ± 1.0
PMMA (atactic, 2 g/l)– α -Al ₂ O ₃	0.40 ± 0.06	1.35 ± 0.20	3.4 ± 1.0
PMMA (isotactic, 2 g/l)– α -Al ₂ O ₃	0.50 ± 0.08	0.37 ± 0.06	0.8 ± 0.2
PMMA (syndiotactic, 2 g/l)– α -Al ₂ O ₃	0.37 ± 0.06	0.66 ± 0.10	1.8 ± 0.5

Table 4
Values of acidic and basic constants of the various PMMA adsorbed on silica

Solid substrate	K_A (kJ/mol)	K_D (kJ/mol)	K_D/K_A
SiO ₂ A130	1.14 ± 0.06	0.37 ± 0.07	0.32 ± 0.05
PMMA(atactic, 20 g/l)–SiO ₂ A130	0.67 ± 0.03	1.18 ± 0.03	1.76 ± 0.07
PMMA(isotactic, 20 g/l)–SiO ₂ A130	0.51 ± 0.05	0.62 ± 0.04	1.21 ± 0.09
PMMA(syndio, 20 g/l)–SiO ₂ A130	0.43 ± 0.04	0.69 ± 0.05	1.61 ± 0.08

PMMA adsorbed on silica are given in Table 4. These results prove the change of the acid and base constants when the tacticity of polymer adsorbed on silica changes. The study of Table 4 also shows that the acidity and basicity of our samples depend on the tacticity of PMMA.

We also studied the effect of the fraction recovery of PMMA adsorbed on alumina or on silica on the acid–base properties. We plotted in Figs. 4 and 5 the variations of K_A and K_D as a function of the recovery fraction of polymer. Figs. 4 and 5 clearly prove that when we reach a monolayer of PMMA adsorbed on alumina or on silica, we approach the physico-chemical properties of PMMA in the bulk phase.

4.2. Specific entropy of the solid substrates

Applying Eq. (9) and using the experimental data obtained by IGC, we determined not only the specific enthalpy but also the specific entropy of adsorption of some polar organic molecules and the various solid substrates (PMMA, SiO_2 , Al_2O_3 , PMMA– SiO_2 and PMMA– Al_2O_3 systems). Results obtained are given in Tables 5 and 6.

Tables 5 and 6 obviously show again the effect of the tacticity of polymer on the superficial properties

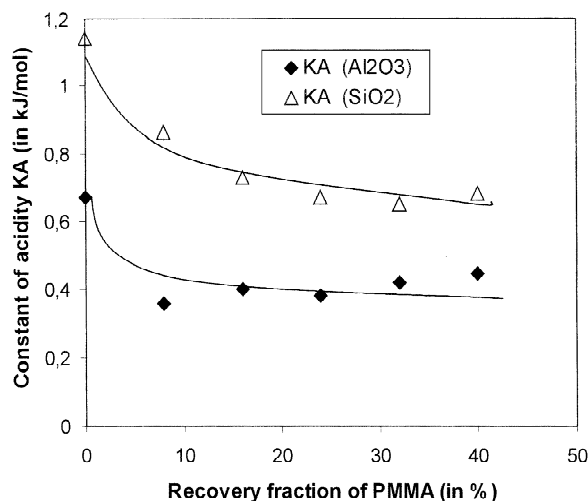


Fig. 4. Evolution of K_A (in kJ/mol) as a function of the recovery fraction of PMMA adsorbed on alumina or silica.

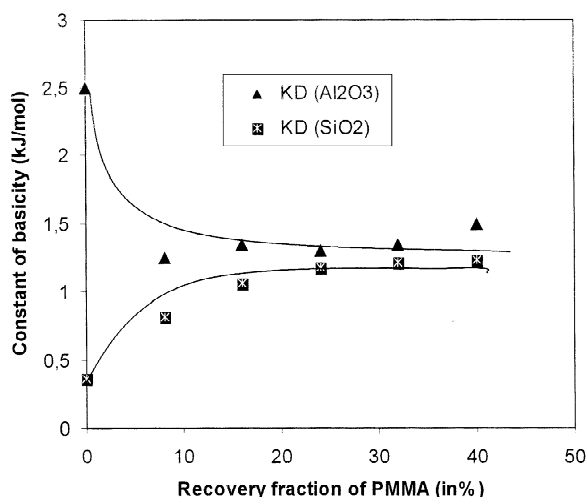


Fig. 5. Evolution of K_D (in kJ/mol) as a function of the recovery fraction of PMMA adsorbed on alumina or silica.

and especially on the specific entropy of interactions between polar molecules and polymers at various tacticities. We observed that ΔS_a^{sp} increases from atactic PMMA–alumina or –silica systems to isotactic PMMA–alumina or –silica systems. We can say that the disorder between polar molecules and polymer adsorbed on alumina or silica follows this classification:

a-PMMA < syndio-PMMA < iso-PMMA.

However, the various adsorbed PMMAs were also classified by decreasing order of their basic character

a-PMMA > syndio-PMMA > iso-PMMA.

It seems that, for more basic PMMA (atactic) adsorbed on solid substrates (as alumina or silica), the disorder between polar probes and PMMA is minimum. Because of the important polar interaction, this leads to the organised surface obtained when organic molecules are adsorbed on atactic PMMA–alumina or –silica. On the other hand, there is a direct correlation between ΔS^{sp} of adsorption and the acid–base properties of the probes. In fact, when the ratio DN/AN of polar molecules increases, ΔS^{sp} decreases (Tables 4 and 5) and the matter state will be more organised.

Table 5

Values of the specific entropy of alumina and of PMMA adsorbed on alumina for various tacticities of polymer

Probes	DN/AN	ΔS_a^{sp} (J K ⁻¹ mol ⁻¹)	S_a^{sp} (J K ⁻¹ mol ⁻¹) of a monolayer PMMA (adsorbed on Al ₂ O ₃)		
			Al ₂ O ₃	Atactic	Syndio
CCl ₄	0	-3±1	-2±0	0	0
CHCl ₃	0	-100±9	-48±6	-14±3	-2±0
CH ₂ Cl ₂	0.22	-73±8	-36±5	-9±2	-1±0
Toluene	2.95	-35±5	-24±4	-15±3	-13±2
Diethyl ether	9.8	-90±7	-46±5	-33±4	-39±5
THF	26.32	-87±7	-49±6	-40±6	-55±6

4.3. A new model for acid–base constants of a solid

4.3.1. Development of a new model

For many solid substrates, especially for polymers and some particular oxides, relation (1) given by $(-\Delta H^{sp}) = K_A DN + K_D AN$ was proved precise enough to obtain the acid–base constants of a solid, with an acceptable accuracy.

By studying some metallic oxides (MgO, ZnO, etc.) and carbon fibres, we corrected relation (1) and proposed a new relationship by adding a third parameter K reflecting the amphoteric character of the oxide according to:

$$(-\Delta H^{sp}) = K_A DN + K_D AN - K DN AN \quad (12)$$

N.B. In the case of polymer powder such as PMMA at various tacticities adsorbed on alumina or silica, we proved that the results obtained by Eqs. (1) and (12) are the same.

By dividing Eq. (12) by AN , we obtain:

$$-\frac{\Delta H^{sp}}{AN} = K_A \cdot \frac{DN}{AN} + K_D - K DN \quad (13)$$

Eq. (13) can be symbolically written as:

$$X_1 = K_D + K_A X_2 - K X_3 \quad (14)$$

where

$$X_1 = -\frac{\Delta H^{sp}}{AN}, \quad X_2 = \frac{DN}{AN}, \quad X_3 = DN \quad \text{and} \\ K = K(K_A, K_D)$$

X_1 , X_2 and X_3 are known for every polar molecule, whereas K_D , K_A and K are the unknowns of the problem.

By using N probes, Eq. (14) will allow us to write the following equations:

$$\sum_{i=1}^N (X_1)_i = K_D N + K_A \sum_{i=1}^N (X_2)_i - K \sum_{i=1}^N (X_3)_i \quad (15)$$

$$\sum_{i=1}^N (X_1 X_2)_i = K_D \sum_{i=1}^N (X_2)_i + K_A \sum_{i=1}^N (X_2)_i^2 - K \sum_{i=1}^N (X_2 X_3)_i \quad (16)$$

$$\sum_{i=1}^N (X_1 X_3)_i = K_D \sum_{i=1}^N (X_3)_i + K_A \sum_{i=1}^N (X_2 X_3)_i - K \sum_{i=1}^N (X_3)_i^2 \quad (17)$$

Table 6

Values of the specific entropy of silica and of PMMA adsorbed on silica for various tacticities of polymer

Probes	DN/AN	ΔS_a^{sp} (J K ⁻¹ mol ⁻¹)	S_a^{sp} (J K ⁻¹ mol ⁻¹) of a monolayer PMMA (adsorbed on Al ₂ O ₃)		
			Al ₂ O ₃	Atactic	Syndio
CCl ₄	0	0	0	0	0
CHCl ₃	0	-3±2	-15±3	-13±3	-12±3
CH ₂ Cl ₂	0.22	-2±0	-3±1	-3±1	-3±1
Toluene	2.95	-3±1	-4±1	-5±1	-6±2
Diethyl ether	9.8	-67±7	-62±7	-41±7	-53±6
THF	26.32	-100±7	-60±7	-46±5	-57±6

We obtain a linear system given by Eqs. (15)–(17) at three unknown numbers: K_D , K_A and K . The matrix representing this linear application is a symmetrical one, so we deduce that the problem (15)–(17) has a unique solution for $N \geq 3$. We applied this method to calculate the acid–base constants of our solid substrates.

4.3.2. Experimental results

By studying other oxides and carbon fibres (treated or untreated), we observed that when we used Eq. (1), the results obtained by this model were very poor (the linear regression coefficient was less than 0.6). However, when we applied our new model given by Eq. (12), the results were improved and the linear regression coefficient was greater than 0.9. Using the previous data obtained by IGC on the given solids, calculations lead to the results of Table 7.

Table 7 allows us to compare the acid–base properties of Monogal, MgO and ZnO: MgO is the more basic oxide. This interesting result was confirmed in a previous study [19] by using the zeta potential technique in aqueous and organic media. Calculations applied on the various carbon fibres allowed us to obtain the results listed in Table 7.

Table 7 also allows us to compare between the acid–base properties of carbon fibres. Coated fibre CF1 is the more basic fibre. Basicity of these fibres can be classified in decreasing order:

CF1 fibre > CF2 fibre > OF fibre > UF fibre

However, the fibres CF1 and CF2 have the same acidity strength, but they are more acidic than the untreated and oxidised fibres.

Table 7
Values of K_A , K_D and K of oxide surfaces using our model

Oxide or fibre	K_A (J/mol)	K_D (J/mol)	K (J/mol)
Monogal	320	810	90
MgO	270	2270	140
ZnO	830	400	70
UF fibre	232	585	4
OF fibre	438	2516	64
CF1 fibre	555	7500	184
CF2 fibre	591	4580	124

5. Discussion

Concerning the effect of the tacticity of the polymer, we proved that we can classify the various adsorbed PMMA by decreasing order of this basic character as:

a-PMMA > syndio-PMMA > iso-PMMA.

This proves that the isotactic polymer strongly interacts with the alumina or silica surface by its basic ester groups [24]. This decreases the basicity of the PMMA–alumina PMMA–silica systems. In the case of syndiotactic PMMA, some basic groups do not interact with alumina or silica and this confers to the covered surface a more pronounced basic character than for isotactic PMMA but less than that of the atactic polymer. The explanations for these results are that interfacial conformational changes of PMMA chain segments arise with a level which depends on tacticity, and that the level of the acid–base interactions of the PMMA side-chain with alumina or silica also depends on tacticity. Indeed, iso-PMMA undergoes more interfacial conformational changes than the other isomers and most of the functional groups of the adsorbed isotactic PMMA are involved in interfacial interactions. Hence, the free functional groups (not involved in acid–base interactions with oxide) probed by IGC are more important for the a- and syndio-PMMA than for the isotactic isomer.

On the other hand, the main opposing fact to a direct transposition of bulk quantities (AN , DN in Eqs. (1) and (12)) to interfacial interactions lies in the discontinuity in the symmetry of the local interactions involving the molecules, when transferring these molecules from the bulk to a rigid surface [5,25]. Because of this situation, steric constraints due to the interfacial structuring of the contacting liquid over few monolayers towards the bulk phase will grow. This local structuring may not allow—for coordination and steric reasons—the donor and acceptor sites apart from the interface to participate and most importantly, to interact as in the bulk phase. Basically, these local structuring and related constraints may be dependent on both the nature and strength of the interaction sites on the solid surface (see for instance the structuring of water along hydrophilic and hydrophobic surfaces [26]).

The empirical acid–base strengths of usual liquids refer, in the concept of Gutmann, to their bulk interactions with arbitrary chosen and exclusively donor or acceptor probes (SbCl_5 and Et_3PO). One can therefore expect these liquid molecules, when confined at the interface with a solid, to have a quite different interaction efficiency for coordination and steric constraint reasons, but also for the more obvious fact that the interacting species are just different from SbCl_5 and Et_3PO . Therefore, regardless of the coordination and steric effects arising from the shift from bulk interactions to confined ones at a solid interface, the AN and DN values cannot simply be transposed, since surface site–liquid interactions are not symmetric like those involving liquid- SbCl_5 or liquid- Et_3PO . Accordingly, the dependence of the reference bulk quantities on both the nature of the interacting species, the local coordination and physical constraints can be taken into account by introducing a correction term to Eq. (1), and Eq. (12) satisfies such a correction as it affords more information on the effectiveness of the interactions involved at the interface.

6. Conclusion

In this part, we showed that inverse gas chromatography at infinite dilution can be strongly used to characterise the superficial and interfacial properties of solid substrates such as oxides, polymers or polymers adsorbed on oxides. Especially, we studied the acid–base properties of silica, alumina, PMMA with different tacticities and PMMA adsorbed on alumina and silica.

A new model concerning the acid–base constants was proposed by introduction of a third parameter K which reflects the amphoteric features of a solid like oxides or carbon fibres. Results obtained by this model are improved.

7. Nomenclature

a	Surface area of molecule
A	Constant depending on the nature of the solid substrate
AN	Acceptor number of electrons

B	Second constant depending on the nature of the solid substrate
C	Constant depending on the reference state of adsorption
DN	Donor number of electrons
DN'	Normalised donor number of electron
D_c	Corrected flow-rate
D_m	Measured flow-rate
j	Correction factor taking into account the compression of a gas
K	Parameter reflecting the amphoteric character of a solid
K_A	Acidic constant of a solid
K_D	Base constant of a solid
N	Number of probes
N	Avogadro number
PZC	Point of Zero Charge
P_0	Vapour pressure of a probe
P_a	Atmospheric pressure
r	Sum of the cationic radius and the oxygen diameter
R	Ideal gas constant
t_0	Zero retention reference time
t_R	Retention time of a probe
T	Absolute temperature
T_c	Column temperature
T_a	Room temperature
V_n	Net retention volume
Z	Formal charge of a cation
γ_s	surface energy of the solid
γ_1^d	Dispersive component of the surface energy of the probe (liquid)
γ_s^d	Dispersive component of the surface energy of the solid
ΔG^0	Free enthalpy of adsorption
ΔG^d	Free enthalpy of adsorption corresponding to dispersive interactions
ΔG^{sp}	Specific free enthalpy
ΔH^{sp}	Specific enthalpy
ΔP	Pressure variation.
ΔS^{sp}	Specific free entropy
η	Viscosity gas

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