# Solid surface mapping by inverse gas chromatography

M.C. Gutiérrez [a,*], S. Osuna [b], I. Baráibar [a]

[a] *Cooperación Bilateral, Subdirección General de Relaciones Institucionales y Política Comercial,
Instituto Nacional de Técnica Aeroespacial, Ctra. Ajalvir, km. 4, 28850, Torrejón de Ardoz, Madrid, Spain*
[b] *Centro de Astrobiología (INTA-CSIC), Ctra. Ajalvir Km. 4, 28850, Torrejón de Ardoz, Madrid, Spain*

**Abstract**

Inverse gas chromatography (IGC) at infinite dilution, is a technique for characterising solid surfaces. Current practice is the injection of *n*-alkane homologous series to obtain the free energy of adsorption of the $CH_2$ group, from which the London component of the solid surface free energy, $\gamma_S^d$, is calculated. A value around $40\,mJ/m^2$ is obtained for poly(ethylene), and $30\,mJ/m^2$ for a clean glass fibre, while the potential surface interactivity of a glass fibre is far greater than that of poly(ethylene). A specific component of the surface, in $mJ/m^2$, should be calculated in order to obtain significant parameters. As applied up to date, when calculating the specific component of the surface energy, the fact that $W_a^{sp}$ energy values are in a totally different scale than AN or DN values is a major drawback. Consequently, Ka and Kb values obtained are in arbitrary energy units, different from those of the London component measured by injecting the *n*-alkane series. This paper proposes a method to obtain Ka and Kb values of the surface in the same energetic scale than the London component. The method enables us to correct the traditional London component of a solid, obtaining a new value, where the amount of $W_{aCH_2}$ accounting for Debye interactions with polar sites, is excluded. As a result, an approach to surface mapping is performed in several different substrate materials. We show results obtained on different solid surfaces: poly(ethylene), clean glass fibre, glass beads, chemically modified glass beads and carbon fibre.
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*Keywords:* Surface free energy; Inverse gas chromatography; Surface mapping

## 1. Introduction

Gas chromatography is an easy technique of separation and/or identification of solutes in a mixture, based on the fact that each solute has a *particular* interaction with the stationary phase, and therefore, the different solutes travel through the column, carried by an inert gas, at different rates. The solutes come out of the column separately and the retention volume $V_R$ of each solute depends on different parameters, among others, the physicochemical properties of the stationary phase and of the solute itself.

Inverse gas chromatography (IGC) takes advantage of this fact, by using a series of solutes (probes), of well known physico-chemical characteristics. Information of the nature of the column can be obtained. from their measured $V_N$ values.

Injecting a minimum vapour amount of solutes, allows us to assume that no solute–solute interaction takes place, only solid–solute interactions occur. In these conditions, Henry's law can be applied, and the proportion of adsorbed solute (and therefore the retention volume $V_R$), is practically independent of the probe concentration [1]

### 1.1. Theoretical background of IGC

The net retention volume, $V_N$, of a solute is related to the standard variation of the free energy of adsorption

$$-\Delta G_A = RT \ln V_N + C \tag{1}$$

where $C$ is a constant that depends on the reference state [2], $R$ is the gas constant and $T$ is the column temperature in K.

According to Fowkes [3], the work of adhesion ($W_a$) between two phases can be considered the as the sum of dispersive and nondispersive (or specific) contributions, as the solid surface energy $\gamma_S$ of any substance can be written as a

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\* Corresponding author. Tel: +34 91 520 1275; fax: +34 91 520 1939.
*E-mail address:* gutierrezhm@inta.es (M.C. Gutiérrez).

sum of dispersive and nondispersive components [4]

$$\gamma_S = \gamma_S^d + \gamma_S^{sp} \tag{2}$$

where $\gamma_S^d$, or the London component of the free energy, is the sum of the free energy of those active non-polar sites, that can only interact with in-coming molecules, with dispersive interactions, and $\gamma_S^{sp}$, or the specific component of the free energy, is the sum of surface free energy, of all other specific active sites of polar nature, with different character and intensity.

### 1.1.1. Calculation of the London component, $\gamma_S^d$, of the free surface energy

When injecting $n$-alkane in a column X, we obtain $\Delta G_{CH_2}$ (free energy of adsorption of a methylene group) from the slope of the line obtained when plotting $\Delta G_A$ versus number of carbon atoms. This work of adhesion, is dominated by dispersive interactions, so the following expression is traditionally used according to Fowkes's expression [4]

$$W_{aCH_2} = W_{aCH_2\,London} = 2(\gamma_{CH_2}^d \times \gamma_S^d)^{1/2} \tag{3}$$

where $\gamma_{CH_2}^d$ is the surface energy of members of $n$-alkane series and $\gamma_S^d$ is the London component of the solid surface. Taking for $\gamma_{CH_2}^d$ the surface energy of members of the $n$-alkane series [5], or that of poly(ethylene), the value $\gamma_S^d$ can be calculated.

### 1.1.2. Calculation of the specific component, $\gamma_S^{sp}$, of the free surface energy

The attempts made up to now for the calculation of this component, have failed to give specific surface energy values in the same scale as $\gamma_S^d$. All methods described in the literature rely on the same philosophy. The free energy of adhesion is plotted versus a *chosen property* of the probes, which is likely to be closely linked to its *capability to interact in a non-specific manner*. The series of $n$-alkanes are included in this plot, which shows a linear relation between the chosen property and the free adhesion energy. The key point is to accept that, for a given polar probe (with a given value in the chosen property), its dispersive work of interaction with the solid stationary phase is the same, that the interaction of the hypothetical n-alkane that has the same value in the chosen property, and therefore, subtracting this work of adhesion from the total work of adhesion of each polar probe, a *specific work of adhesion, Isp*, is calculated for each probe. Among the chosen properties proposed by different authors are: $\log P^0$ [6], $a(\gamma_L^d)1/2$ [5], boiling temperatures $T_b$ [7], molecular refraction $P_D$ [8], polarizability function [9]. A new topology index, $\chi_T$, is defined for this application [10]. We proposed a method [11] in the same line, where the chosen property was the Kóvats index of the probe on a non-polar column of poly(ethylene).

$Ka_S$ and $Kb_S$, acid and base "numbers" of the solid surface, were calculated by plotting Isp/AN of each polar probe,

versus DN/AN. The slope being $Ka_S$, and $Kb_S$ the intercept, assuming the widely used equation

$$Isp = Ka_S \times DN_{probe} + Kb_S \times AN_{probe} \tag{4}$$

where Isp is the specific work of adhesion of each probe, and AN and DN the donor acceptor numbers as found in the literature [12,13]. We think that in most methods, too much free energy of adsorption is subtracted from the total interaction in order to find the specific fraction. With the exception of the approaches of Donnet et al. [9], Vidal et al. [14], and Brendlé and Papirer [10], all properties are greatly conditioned by not only dispersive interactions between molecules, but also by interactions of polar character.

Another important drawback of this methodology is that, although in principle DN/AN are meaningful figures, provided that donor and acceptor numbers are normalised in the same scale, *Isp energy values are in a totally different scale than AN or DN values*. The consequence is that the plot of Isp/AN versus DN/AN will produce Ka and Kb data in *arbitrary energy units* which have only a limited comparative value.

### 1.2. A novel approach proposed for surface energy splitting, by IGC

Van der Waals attractions are widely accepted to be of three main types [15]:

(a) Keesom interactions (dipole–dipole).
(b) Debye interactions (dipole-induced dipole).
(c) London dispersion (induced dipole-induced dipole).

Up to now, Debye interactions between probes and solid stationary phase have been ignored. Our proposal is based on the inclusion of these in all calculations.

If we separate electron donor and electron acceptor sites in a solid surface, Eq. (2) takes the form:

$$\gamma_S = \gamma_S^d + \gamma_S^A + \gamma_S^B \tag{5}$$

in which most other type of interactions are enclosed.

Probes also have, in most cases, both types of interactivity potential, represented by R–X, where R represents the non-polar part of the molecule, and X represents the active point/s.

The total work of adsorption of each probe L, with an heterogeneous solid surface S, will be the sum of the following terms:

$$
\begin{aligned}
W_{a\,Total}(L-S) = {} & W_{a\,London}(R-\gamma_S^d) \\
& + W_{a\,Debye}(R-\gamma_S^{A\,and\,B}) \\
& + W_{a\,Debye}(X-\gamma_S^d) \\
& + W_{a\,Keesom}(X-\gamma_S^{A\,and\,B}) \tag{6}
\end{aligned}
$$

where $W_{a\,London}(R-\gamma_S^d)$ represents the work of interaction of the non-specific part of the probe molecule with the non-specific sites of the solid surface, $W_{a\,Keesom}$

$(X - \gamma_S^{A \text{ and } B})$ represents the acid base interaction between the probe molecule and the specific sites of the solid surface, and the other two terms account for the Debye interactions (dipole-induced dipole) between probes and solid.

For $W_{a \text{ London}}(R - \gamma_S^d)$, and $W_{a \text{ Keesom}}(X - \gamma_S^{A \text{ and } B})$, we apply analogous expressions to Eqs. (3) and (4). For $W_{a \text{ Debye}}(R - \gamma_S^{A \text{ and } B})$ and $W_{a \text{ Debye}}(X - \gamma_S^d)$ we apply simple expressions of the type shown in Eq. (9), therefore:

$$W_{a \text{ London}}(R - \gamma_S^d) = 2 \times (\gamma_L^d \times \gamma_S^d)^{1/2} \tag{7}$$

$$W_{a \text{ Keesom}}(X - \gamma_S^{A \text{ and } B}) = (\gamma_S^A \times DN_X) + (\gamma_S^B \times AN_X) \tag{8}$$

$$W_{a \text{ Debye}}(L - S) = \gamma_L^d \times (\gamma_S^A + \gamma_S^B) + \gamma_S^d \times (AN_X + DN_X) \tag{9}$$

This is done based on the experimental data obtained when polar probes interact with a non-polar solid surface, or reference solid, of poly(ethylene) (PE).

## 2. Experimental

The instrument used is a Perkin-Elmer Autosystem. Flame ionisation detection is used in the highest sensitive range. The amount of probes injected is $10^{-5}$ to $0.05 \text{ cm}^3$ of gas from the vessel's headspace, working at infinite dilution. Helium is used as carrier gas, and flow rates are in the range $3–30 \text{ cm}^3/\text{min}$ for each solid stationary phase studied. Void retention time, $t_0$, is calculated by mathematical tailoring of expression:

$$(t_E - A) = \exp(B + Cn) \tag{10}$$

where $t_E$ is the elution time, therefore for $n = 0$, $t_0 = A + \exp B$ which would be the retention time of an hypothetical $n$-alkane with 0 number of carbon atoms. The retention time of each member of the series of $n$-alkanes is then, $t_{Ri} = t_{Ei} - t_0$.

$V_N$ are *net retention volumes at a reference temperature of 25 °C*, calculated through the carrier gas flow rate, measured at the column outlet at ambient pressure and room temperature, and corrected to 25 °C.

Materials studied are:

The reference material is ground poly(ethylene) (1–5 μm diameter grain size) provided by courtesy of Repsol YPF.
E-Glass fibre solvent extracted, provided by Cristalera Española.
E-Glass beads solvent extracted, provided by Sovitec Ibérica, 600–800 μm diameter.
These glass beads after in situ reaction, at 120 °C, with aminopropyl-trimethoxysilane.
Non-sized AS4 carbon fibre of Hexcel Composites.
All solvents are from Merck-Schuchard, HPLC or zur Analysis.

All materials were introduced in PTFE tubing with 1/4 in. or 1/8 in. outer diameter.

## 3. Methods and applications

The proposed method deals with several non-solved problems in the following way.

### 3.1. The area problem

All terms of Eq. (6) have to be expressed in *work of adhesion per unit area*, and all free surface energy values have also to be expressed in *free surface energy per unit area*. An estimation of *contact areas* is then required.

Several area sets for $n$-alkanes and for polar probes are found in the literature, used by scientists for IGC calculations. Some are based on geometrical molecular models and others are based on experimental adsorption data. There is no clear correlation between them. In Fig. 1, we show some of these area sets for polar probes. We include those calculated by us as described below.

Recently Hamieh and Schultz [16] recalculated and reviewed various models in order to calculate the molecular areas of some non-polar and polar probes and proposed a chromatographic method to do it.

We think that in all cases, chromatographic methods provide higher molecular contact areas of polar molecules, because of the ignored Debye interactions.

We make an estimation of the area of all probes, both polar and non-polar. This is done with the help of atomic radii, and bond lengths of diatomic molecules found in the literature [17]. We use the generally accepted value for the $\text{area}_{CH_2}$ of $0.06 \text{ nm}^2$. Another molecule, or a group of atoms, is supposed to occupy (when adsorbed on a solid surface) the sum of the areas of their constituting atoms. This approximation is likely to be valid in the case of simple molecules like those used as probes in IGC. The ratio ($\text{area}_{\text{molecule}}/\text{area}_{CH_2}$) is calculated by building a scale with the *area of the circumferences, as the shadow on the plane* of atoms considered as spheres. These molecules are supposed to show a shadow by addition of the shadows of constituting atoms.
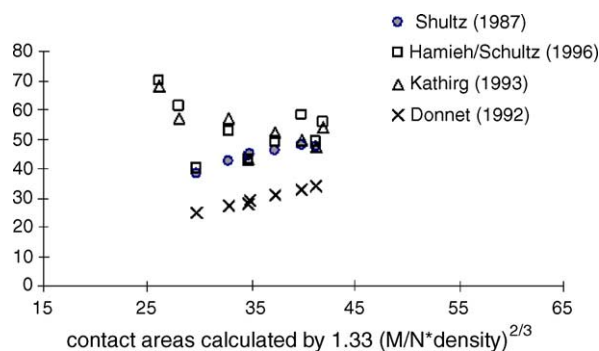


Fig. 1. Some sets of *area of interaction* of polar probes found in the literature, $\times 10^2 \text{ nm}^2$.

### 3.2. Units for AN and DN values

Polar probes often used for the evaluation of the acid or basic character of the solid stationary phase consist of volatile molecules like: chloroform, acetone, ethyl acetate, diethyl ether, methylene chloride, tetrahydrofuran, acetonitrile, alcohols, etc. Their electronic donor and acceptor character is given by Gutmann [12] as DN and AN values. The DN values measure the energy of a co-ordinate bond between a donor atom and the Sb of $SbCl_5$, its value is given in kcal/mol. AN is derived from relative $^{31}P$ NMR chemical shifts in $Et_3PO$, when dissolved in the acid species being evaluated, and is a dimensionless number. Riddle and Fowkes [13], made corrections to Gutmann's original AN values for the Van der Waals contribution to the chemical shift, on the basis of the determination of the $\gamma^d$ values yielded from measurement of the surface and interfacial tensions of the test liquids. Values of $(AN - AN^d)$ are given, which we take as the corrected Gutmann's shift values. But if AN and DN values are not normalised to the same scale, the results of acid–base interactions would turn out to be meaningless. This is done according to Mukhopadhyay and Schreiber [18] through the DN value of $Et_3PO$ (the AN reference molecule) that is 40 kcal/mol. AN values can be recalculated in the same scale as DN original reported values.

DN and AN (Gutmann's scale) or $AN^*$ (Riddle–Fowkes's scale), used in this work are given in Table 1.

Up to now, the values in Table 1 are used unmodified in most recent IGC studies [19–21].

AN and DN numbers are supposed to be in the same energy units, *but not in Isp energy units*. When we apply Eq. (4) for acid–base components of the solid surface, by IGC, only DN/AN data have physical meaning. Recalculation of AN and DN numbers, in the same energy units as the work of adsorption measured by chromatography, is needed, assuming that DN/AN reported values are correct.

This is done in this work by measuring adsorption energies of all polar probes on a reference column made of poly(ethylene), PE. Fortunately two experimental observations concur to fulfil our purpose:

(a) one is the fact that the adsorption of all probes on poly(ethylene), if expressed in $W_{a\,Probe}/W_{a\,CH_2}$ (which we call $CH_2$ *index*, $I_x$) is non-temperature dependent.
(b) the other lucky fact is that on PE, (being unable to interact with Keesom forces) we obtain a line when plotting $W_{a\,Probe}/AN$ versus DN/AN. We understand that Debye forces dominate these interactions, and are responsible for this phenomenon, thus Eqs. (9) and (6) are reduced to:

$$W_{a\,Debye}(L - PE) = \gamma_{PE}^d \times (AN + DN) \qquad (11)$$

$$W_{a\,Total}(L - PE) = 2 \times (\gamma_L^d \times \gamma_{PE}^d)^{1/2} + \gamma_{PE}^d \times (AN + DN) \qquad (12)$$

Provided we can estimate $\gamma_L^d$, of each probe, $(AN + DN)$ in adsorption energy units, can be calculated.

With DN/AN values taken from the literature, AN and DN values derived from measured adsorption energies on PE can be recalculated.

### 3.3. Calculation methodology of partial surface energy contributions

Once AN and DN values of each probe are calculated from adsorption on PE, we are in a position to plot $W_{a\,Keesom}/AN$ versus DN/AN in the same energy units, when studying an heterogeneous solid surface.

We have chosen those probes in which the splitting of the polar and non-polar part of the molecule are more obvious; these are acetone, ethyl acetate, tetrahydrofuran, acetonitrile, methanol and ethanol. We assume that $\gamma_L^d$ of the non-polar part of the probe, *by unit area*, is the same as $\gamma_L^d$ of *n*-alkanes and the same as $\gamma_{PE}^d$.

A system of six equations is established, one for each probe, with Eq. (6), using Eqs. (7)–(9). We optimise, to minimum quadratic, $\sum(W_{a\,exper.} - W_{a\,calc.})$, thus obtaining optimum values of $\gamma_S^d$, $\gamma_S^A$ and $\gamma_S^B$.

Table 1
Donor and acceptor numbers of polar probes commonly used, according to Gutmann's [12], Fowkes' [13] normalised as Mukhopadhyay [18]

| Polar probe | Gutmann | | Fowkes | Gutmann | Fowkes |
|---|---|---|---|---|---|
| | AN n.u. | DN n.u. | $AN^*$ n.u. | DN/AN | DN/AN* |
| Chloroform | 23.1 | 0 | 18.7 | 0.00 | 0 |
| Acetone | 12.5 | 42.5 | 8.7 | 3.40 | 4.89 |
| Ethyl acetate | 9.3 | 42.8 | 5.3 | 4.60 | 8.07 |
| Ethyl ether | 3.9 | 48.0 | 4.9 | 12.31 | 9.80 |
| THF | 8.0 | 50.0 | 1.9 | 6.25 | 26.32 |
| Acetonitrile | 19.3 | 35.3 | 16.3 | 1.83 | 2.16 |
| Methylene chloride | 20.4 | 0 | 13.5 | 0.00 | 0 |
| Methanol | 41.3 | 47.5 | 41.7 | 1.15 | 1.14 |
| Ethanol | 37.1 | 50.0 | 35.9 | 1.35 | 1.39 |
| 1-Butanol | 36.8 | | 31.7 | | |

Table 2
Calculated areas of polar molecules and radicals

| Atom or group | Area of shadow $\times 10^2$ (nm$^2$) | Area$_{molecule}$/area$_{CH_2}$ | Calculated area $\times 10^2$ (nm$^2$) | Non-polar fraction $\times 10^2$ (nm$^2$) |
|---|---|---|---|---|
| CH$_2$– | 2.52 | 1.000 | 6.00 | 6.00 |
| CH$_3$– | 2.86 | 1.133 | 6.80 | 6.80 |
| Methane | 3.19 | 1.266 | 7.59 | 7.59 |
| Ethane | 5.71 | 2.266 | 13.59 | 13.59 |
| Propane | 8.23 | 3.266 | 19.59 | 19.59 |
| Butane | 10.75 | 4.266 | 25.59 | 25.59 |
| Pentane | 13.27 | 5.266 | 31.59 | 31.59 |
| Hexane | 15.79 | 6.266 | 37.59 | 37.59 |
| Heptane | 18.31 | 7.266 | 43.59 | 43.59 |
| Octane | 20.83 | 8.266 | 49.59 | 49.59 |
| Nonane | 23.35 | 9.266 | 55.59 | 55.59 |
| Decane | 25.87 | 10.266 | 61.59 | 61.59 |
| Undecane | 28.39 | 11.266 | 67.59 | 67.59 |
| Dodecane | 30.91 | 12.266 | 73.59 | 73.59 |
| Hexadecane | 41.00 | 16.266 | 97.59 | 97.59 |
| Chloroform | 11.50 | 4.561 | 27.37 | 5.20 |
| Acetone | 8.26 | 3.279 | 19.67 | 13.59 |
| Ethyl acetate | 12.17 | 4.827 | 28.96 | 19.59 |
| Ethyl ether | 12.13 | 4.814 | 28.89 | 25.59 |
| THF | 11.46 | 4.549 | 27.29 | 24.00 |
| Acetonitrile | 5.34 | 2.120 | 12.72 | 6.80 |
| Methylene chloride | 8.73 | 3.463 | 20.78 | 6.00 |
| 2-Propanol | 9.28 | 3.681 | 22.89 | 18.80 |
| Methanol | 4.57 | 1.814 | 10.89 | 6.80 |
| Ethanol | 7.09 | 2.814 | 16.89 | 12.80 |
| 1-Propanol | 9.61 | 3.814 | 22.89 | 18.80 |
| 1-Butanol | 12.13 | 4.814 | 28.89 | 24.80 |
| 1-Pentanol | 14.65 | 5.814 | 34.89 | 30.80 |
| 1-Hexanol | 17.17 | 6.814 | 40.89 | 36.80 |
| 1-Heptanol | 19.70 | 7.814 | 46.89 | 42.80 |

## 4. Results and discussion

### 4.1. Areas of interaction of polar and non-polar probes

Bond lengths of covalent molecules are taken from literature [17] from which the approximate area of the atoms, groups or molecules are estimated. These are normalised to the generally accepted value of 0.06 nm$^2$ for the methylene group. The approximate area values calculated by us for *n*-alkanes and all polar probes used, are shown in Table 2.

Correlation between the calculated areas and those given by Dorris et al. [22] is fairly good, as Fig. 2 shows.

### 4.2. Interaction of polar probes with poly(ethylene)

The work of interaction $W_a$ of a molecule of the *n*-alkane series with the surface of poly(ethylene) is obtained by Eq. (1). The plot of $W_a$ of the series of *n*-alkanes, RH, versus the *equivalent number of* CH$_2$ = area$_{molecule}$/area$_{CH_2}$ gives a line. The slope of this line is $W_{a\,CH_2}$. Considering that the surface energy of both *n*-alkane molecules and poly(ethylene) are equal, $\gamma_{PE} = \gamma_{RH}$, we can calculate them with Eq. (3).

The work of interaction $W_a$ of a polar molecule with the surface of poly(ethylene) is obtained with Eq. (1). $W_a/W_{a\,CH_2}$ is the work of adsorption expressed in an equivalent *CH$_2$ number, or index*, $I_{PE}$. This value is quasi non-temperature dependant, as is shown in Fig. 3.

The interaction of these polar molecules with PE is dominated by Debye interactions. The plot of $W_a$/AN versus DN/AN gives a line for most polar molecules, as shown in Fig. 4.

We correct DN/AN with equations of these lines. We calculate, with Eq. (3), $\gamma_L^d$ *per 0.06 nm$^2$ of each of the six selected polar probes*, assuming that the alkyl radical of each polar molecule has the same $\gamma_L^d$ of the hypothetical *n*-alkane of the
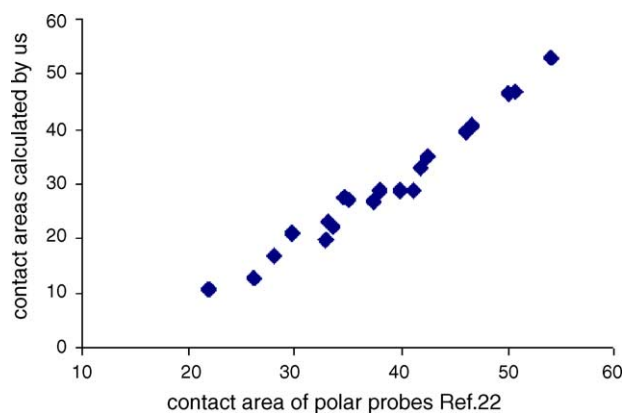
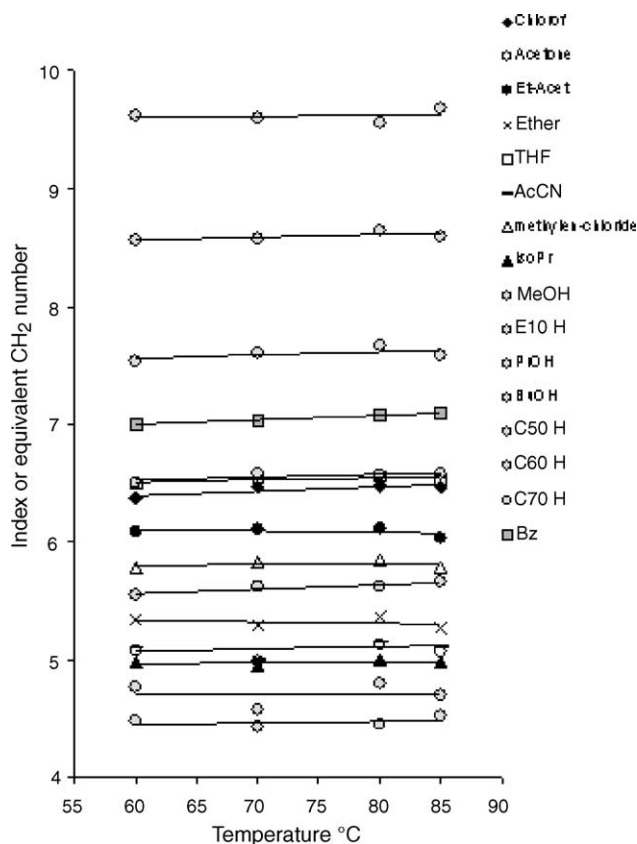Fig. 2. Correlation of calculated areas with those of Ref. [22].

Fig. 3. Index, or equivalent $CH_2$ number, of polar probes on poly(ethylene), $I_{PE}$.

Table 3
Calculated $\gamma_L^d$ of polar molecules expressed in $I_{PE}$/0.06 $nm^2$

| Atom or group | $\gamma_L^d$ in $I_{PE}$ units/0.06 $nm^2$ |
|---|---|
| $CH_2-$ | 0.500 |
| Poly(ethylene) | 0.500 |
| Acetone | 0.346 |
| Ethyl acetate | 0.338 |
| THF | 0.440 |
| Acetonitrile | 0.267 |
| Methanol | 0.312 |
| Ethanol | 0.379 |
| Ethyl ether | 0.443 |
| 2-Propanol | 0.425 |

### 4.3. Interaction of n-alkanes and polar probes with an heterogeneous surface X

$W_{a\,molecule}$ are experimentally obtained in kJ/mol from retention volumes. We obtain the index by dividing by $W_{a\,CH_2}$ in kJ/mol. This index is exclusive of the column X ($I_X$). To obtain the adsorption energy in $I_X$/0.06 $nm^2$, we must consider the estimated areas in $nm^2$. To apply $\gamma_L^d$, AN and DN values of Tables 3 and 4, these must be converted to the same energy units, $I_X$/0.06 $nm^2$ using Eq. (13)

$$W_a(I_X) = W_a(I_{PE})$$
$$\times (W_{a\,CH_2}\,in\,kJ/mol\,on\,PE/\,W_{a\,CH_2}\,in\,kJ/mol\,on\,X)$$

$$(13)$$

We are able to establish six equations, one for each selected polar probe according to Eqs. (6)–(9). Optimum $\gamma_S^d$, $\gamma_S^A$ and $\gamma_S^B$ are obtained in $I_X$ units per 0.06 $nm^2$, easily convertible to kJ/mol and mJ/$m^2$. In Tables 5 and 6 we show the results obtained for several solid materials, together with the traditional London component value obtained exclusively from $W_{a\,CH_2}$, using AN values of Riddle–Fowkes' or Gutmann's scale respectively.

From Tables 5 and 6 we can see the non-polar character of PE, the polar character of clean glass material, and how acidic sites disappear when chemical reaction of the surface with aminopropyl ethoxysilane takes place. We can also appreciate the total value of the surface energy and establish that, energetically speaking:

C fibre > glass beads > glass fibre

> modified glass beads > polyethylene

Which is not the order we would obtain from the traditional London component.

### 4.4. Validation of the method

This method relies on of $\gamma_L^d$, AN and DN values derived from the interaction polar probes on PE. It is necessary to check if, in other materials, the experimental values and those derived from the proposed calculations above fit. In

same area. We divide this value by the calculated area of the probe and multiply this value by 0.06 $nm^2$ (the area of the methylene group), thus obtaining for the six selected probes the following values shown in Table 3.

We calculate (AN + DN) of each polar probe in $I_{PE}$ units/0.06 $nm^2$ with Eq. (12), where all magnitudes are given in those units. DN/AN values of the literature are used to calculate AN and DN values in this same energy scale. This values are given in Table 4.
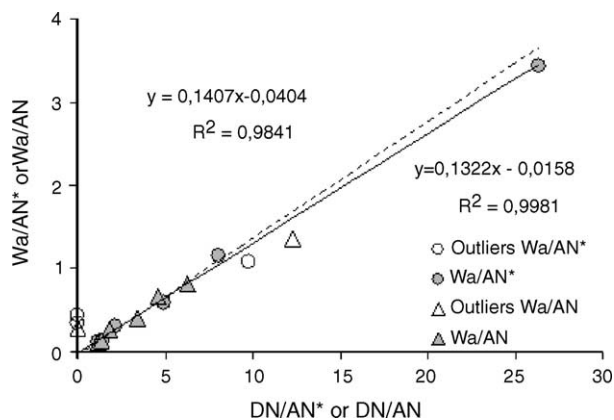


Fig. 4. Debye interaction of polar probes on PE using AN values of Refs. [12,13].

Table 4
Recalculated AN and DN values of polar molecules, in $I_{PE}/0.06\,nm^2$

|  | AN$^*$ $I_{PE}$ units per 0.06 nm$^2$ | DN$^*$ $I_{PE}$ units per 0.06 nm$^2$ | AN $I_{PE}$ units per 0.06 nm$^2$ | DN $I_{PE}$ units per 0.06 nm$^2$ |
|---|---|---|---|---|
| Polyethylene | 0 | 0 | 0 | 0 |
| *n*-Alkane | 0 | 0 | 0 | 0 |
| Acetone | 0.2570 | 1.1578 | 0.3405 | 1.0743 |
| Ethyl acetate | 0.0889 | 0.7807 | 0.1468 | 0.7228 |
| THF | 0.0368 | 0.9634 | 0.1409 | 0.8593 |
| Acetonitrile | 0.9564 | 2.3643 | 1.0529 | 2.2679 |
| Methanol | 1.7195 | 1.5888 | 1.6135 | 1.6947 |
| Ethanol | 0.7568 | 0.8392 | 0.7299 | 0.8661 |
| Ethyl ether | 0.0341 | 0.2827 | 0.0290 | 0.2878 |
| 2-Propanol | 0.3656 | 0.4782 | 0.3610 | 0.4828 |

AN$^*$ and DN$^*$ are derived of Riddle–Fowkes' scale, AN and DN are derived of Gutmann's scale.

Table 5
Calculated $\gamma_S$ components of several solid materials studied, using new AN$^*$ and DN$^*$ values

| Materials | Total $\gamma_S^d$ (mJ/m$^2$) | New $\gamma_S^d$ (mJ/m$^2$) | $\gamma_S^A$ (mJ/m$^2$) | $\gamma_S^B$ (mJ/m$^2$) | Total $\gamma_S$ (mJ/m$^2$) |
|---|---|---|---|---|---|
| Polyethylene 90° | 39 | 39 | 0 | 0 | 39 |
| Glass fibre 90° | 29 | 0 | 56 | 175 | 232 |
| Glass beads 90° | 29 | 0 | 67 | 182 | 248 |
| Modified glass beads 90° | 27 | 27 | 0 | 74 | 101 |
| Unsized carbon fibre 90° | 61 | 1 | 84 | 176 | 261 |

Table 6
Calculated $\gamma_S$ components of several solid materials studied, using new AN and DN values

| Materials | Total $\gamma_S^d$ (mJ/m$^2$) | New $\gamma_S^d$ (mJ/m$^2$) | $\gamma_S^A$ (mJ/m$^2$) | $\gamma_S^B$ (mJ/m$^2$) | Total $\gamma_S$ (mJ/m$^2$) |
|---|---|---|---|---|---|
| Polyethylene 90° | 39 | 39 | 0 | 0 | 39 |
| Glass fibre 90° | 29 | 0 | 42 | 190 | 233 |
| Glass beads 90° | 29 | 1 | 43 | 201 | 246 |
| Modified glass beads 90° | 27 | 22 | 0 | 84 | 106 |
| Unsized carbon fibre 90° | 61 | 2 | 65 | 190 | 257 |

Table 7
Reliability of the method using new AN$^*$ and DN$^*$ values

| Materials adsorption, $I_x$ | PE 90° | | Glass fibre 90° | | Glass b 90° | | Modified glass beads | | C fibre 90° | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Exper. | Calc. | Exper. | Calc. | Exper. | Calc. | Exper. | Calc. | Exper. | Calc. |
| Acetone | 5.04 | 5.05 | 12.08 | 10.67 | 14.19 | 11.85 | 8.16 | 7.79 | 7.22 | 6.60 |
| Ethyl acetate | 6.07 | 6.07 | 13.28 | 11.39 | 15.38 | 12.66 | 8.43 | 8.94 | 7.81 | 7.18 |
| THF | 6.54 | 6.55 | 12.28 | 12.65 | 13.63 | 14.12 | 8.33 | 9.56 | 7.52 | 8.05 |
| Acetonitrile | 5.07 | 5.08 | 12.92 | 13.15 | 13.70 | 14.53 | 8.82 | 8.68 | 7.71 | 7.85 |
| Methanol | 4.43 | 4.44 | 12.20 | 14.36 | 13.50 | 15.50 | 9.89 | 9.57 | 7.28 | 7.93 |
| Ethanol | 4.70 | 4.70 | 12.90 | 12.88 | 14.33 | 13.94 | 9.35 | 9.14 | 7.86 | 7.30 |
| Ethyl ether[a] | 5.29 | 5.30 | 8.92 | 10.25 | 10.45 | 11.20 | 6.26 | 8.49 | 5.65 | 6.23 |
| 2-Propanol[a] | 4.95 | 4.95 | 12.80 | 11.93 | 14.96 | 12.94 | 8.49 | 9.00 | 8.11 | 6.90 |

[a] Not used in the equations system.

Table 8
Reliability of the method using new AN and DN values

| Materials adsorption, $I_x$ | PE 90° | | Glass fibre 90° | | Glass beads 90° | | Modified glass beads | | C fibre 90° | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Exper. | Calc. | Exper. | Calc. | Exper. | Calc. | Exper. | Calc. | Exper. | Calc. |
| Acetone | 5.04 | 5.05 | 12.08 | 10.68 | 14.19 | 11.91 | 8.16 | 7.95 | 7.22 | 6.65 |
| Ethyl acetate | 6.07 | 6.07 | 13.28 | 11.38 | 15.38 | 12.82 | 8.43 | 9.04 | 7.81 | 7.28 |
| THF | 6.54 | 6.55 | 12.28 | 12.86 | 13.63 | 14.51 | 8.33 | 9.93 | 7.52 | 8.24 |
| Acetonitrile | 5.07 | 5.08 | 12.92 | 12.99 | 13.70 | 14.17 | 8.82 | 8.74 | 7.71 | 7.71 |
| Methanol | 4.43 | 4.44 | 12.20 | 14.00 | 13.50 | 15.24 | 9.89 | 9.31 | 7.28 | 7.84 |
| Ethanol | 4.70 | 4.70 | 12.90 | 12.69 | 14.33 | 14.01 | 9.35 | 9.01 | 7.86 | 7.35 |
| Ethyl ether[a] | 5.29 | 5.30 | 8.92 | 9.94 | 10.45 | 11.44 | 6.26 | 8.34 | 5.65 | 6.38 |
| 2-Propanol[a] | 4.95 | 4.95 | 12.80 | 11.84 | 14.96 | 13.27 | 8.49 | 8.95 | 8.11 | 7.07 |

[a] Not used in the equations system.

Tables 7 and 8 we give $W_{\text{probe calc.}}$ and $W_{\text{probe exper.}}$, to compare, by using Riddle–Fowkes and Gutmann scales.

## 5. Conclusions

(1) We can conclude from the results found that the *traditional total London component* of the surface is mainly an indication of the *concentration of active sites* rather than real information of their energetic activity.

(2) In all equations we use work of adhesion per unit area. Therefore we make an estimation of areas of polar probes based on bond lengths.

(3) We propose new values of AN and DN for polar probes taking poly(ethylene) as reference material and expressed in index numbers.

(4) Using this methodology, we show an approximate surface map of poly(ethylene), clean glass fibre, glass beads, modified glass beads and carbon fibre, and a ranking order in surface energy.

## Acknowledgements

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