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Inverse gas chromatography: a new approach to the estimation of specific interactions

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Abstract

Inverse gas chromatography (IGC) has proved to be a powerful tool for characterisation of solid surfaces, particularly those that cannot be easily studied by other methods, like fibres or powders. One of the magnitudes to be measured by this method is the London component of the surface free energy, which denotes the ability of the surface to interact with external material through Van der Waals forces. This value, is determined by measuring the retention volumes of the series of *n*-alkanes. The other interesting magnitude is the *polar* character of the surface energy. Several methods are described in the literature to evaluate this *polarity* or *specific component* of the surface energy, not all giving concordant results. In this paper a method is proposed for the evaluation of this *specific component* of the surface energy, based on the fact, that the shift of Kóvats index of polar compounds in a column, taking as reference a non polar column, is directly in relation with the polarity of the column. Some data are given of interactions obtained with some of the polar probes with previously described methods and the new one. The study material is several carbon fibres, cured and uncured epoxy resins, two modified polyethylene samples and a commercial SP100 column. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many technical and industrial problems today, depend on interface interactions. That is the case in reinforcement–matrix interaction control, in all types of composite materials, or the compatibility of coatings with substrates when protective layers must be applied to sensitive materials, or the effectiveness of adhesives etc. The deep knowledge of the surface, is one objective of many research efforts.

Gas chromatography (GC) is a simple technique for the 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 elute out of the column separately and the retention volume, V_R , of each solute, depends on different parameters, among others, the nature of the stationary phase and the nature of the solute.

Inverse gas chromatography (IGC) takes advantage of this fact, by using a series of solutes (probes), of well known physicochemical characteristics. By introducing them into the column, and measuring their V_R , valuable information of the nature of the column can be obtained, in this case the column materials under investigation.

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2. Theory

2.1. IGC at infinite dilution

Injecting a minimum vapour amount of solutes, in the limit of flame ionization detection (FID) sensitivity, allows one to assume that no solute–solute interactions take place, and only solid–solute interactions occur. Under these conditions, Henry's law can be applied and the proportion of adsorbed solute, and therefore V_R , is practically independent of the probe concentration [1,2]

The retention volume (V_R) of a solute is related to standard variation of the free energy of adsorption according to

$$-\Delta G_A = RT \ln V_R + C \quad (1)$$

where C is a constant that depends on the reference state [3], R is the gas constant and T is the column temperature in K. The free energy of adsorption, as a first approximation, can be linked with the work of adhesion W_A between the vapour probe (adsorbate) and the solid stationary phase per unit surface area, as follows

$$-\Delta G_A = NaW_A \quad (2)$$

where N is Avogadro's number and a is the area of interaction, of the probe.

According to Fowkes [4], the work of adsorption between a gas and a solid surface, can be split into two terms

$$W_A = W_A^D + W_A^{SP} \quad (3)$$

with W_A^D denoting the weak dispersive interactions of Van der Waals forces, and W_A^{SP} including other types of interactions, mainly polar, like acid–base interactions, hydrogen bonding, π bonding etc. Subsequently, the variation of free energy of adsorption in the GC column, and therefore V_R , can also be split similarly.

The solid surface is a set of different accessible active sites of different nature and heterogeneous character. The surface energy, γ_s , is the sum of the free energy of all of those active sites. Generally, γ_s can be split in two components

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (4)$$

where γ_s^d , or the London component of the free energy, is the sum of the free energy of those active sites non-polar, that can only interact with in-coming molecules, with dispersive interactions, and γ_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.

2.2. Determination of the dispersive component, γ_s^d

When n -alkanes are employed as probes, the work of adhesion is dominated by dispersive interactions at the interface, Eq. (3) is reduced to $W_A = W_A^D$, and according to Fowkes's expression [5]:

$$W_A = 2(\gamma_s^d \gamma_L^d)^{1/2} \quad (5)$$

where γ_L^d is the dispersive component of the free energy of the adsorbate and in the case of n -alkanes, the free energy and γ_s^d is the London component of the solid surface free energy.

The retention volumes of n -alkanes will give information about the capability of the solid surface of interacting with non-polar material. Two methods are described in the literature to access to the γ_s^d value of the solid stationary phase.

The method of Dorris and Gray [3] determined γ_s^d from the slope (free energy of adsorption of a methylene group) of the line obtained when plotting ΔG_A , versus number of carbon atoms, of n -alkanes. Eqs. (2) and (5) will allow one to obtain γ_s^d :

$$\gamma_s^d = \Delta G_{CH_2}^2 / 4N^2 a_{CH_2}^2 \gamma_{CH_2} \quad (6)$$

where γ_{CH_2} is the surface energy of polyethylene (35.6 mJ/m², and a_{CH_2} is the area covered by a methylene group (6 Å²) [6].

Schultz et al. [7] made a plot of ΔG_A versus $a(\gamma_L^d)^{1/2}$ of the series of n -alkanes. The combination of Eqs. (1), (2) and (5) gives

$$RT \ln V_R = 2N(\gamma_s^d)^{1/2} a(\gamma_L^d)^{1/2} + C \quad (7)$$

From the slope of the obtained line, γ_s^d can also be calculated.

Both methods use the areas of n -alkanes given by Avgul et al. [6]. The values obtained by these methods are fairly concordant, but we consider more

reliable the Schultz method, as the London component takes into consideration not only one value of γ_L^d , as reference, but also a series of values determined by methods other than GC.

In this paper we use the method of Gray but γ_{CH_2} , is calculated plotting $a(\gamma_L^d)^{1/2}$ versus the number of carbon atoms of the series of *n*-alkanes. The slope of the line gives us a value of 36.71 mJ/m² for γ_{CH_2} , when accepting the areas of *n*-alkanes of Ref. [6].

2.3. Determination of the specific component of the surface energy, γ_s^{sp}

When polar probes are used as adsorbates, both dispersive and specific interactions take place between the probe and the solid stationary phase. From the measured values of retention volumes, V_R , the work of adhesion, W_A , can be calculated with Eqs. (1) and (2). In Eq. (3), we assume that both interactions are additive. If a method is found to evaluate W_A^D of each polar molecule, with Eq. (3), W_A^{SP} , the specific interaction, of each polar probe can be calculated.

Several methods have been described to split W_A in these two components. The difference between them is the definition of the discerning criteria to subtract the dispersive interaction from the total interaction of each polar probe.

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 in close relation with the *dispersive potential interactivity* of the molecule. The series of *n*-alkanes are included in this plot, which show a linear relation between the chosen property and the free energy of adhesion.

The key point is to accept that, for a given polar probe, with a given value in the chosen characteristic, its dispersive work of interaction with the solid stationary phase, is the same, that the interaction of the hypothetical *n*-alkane with the same value in the chosen property.

Among the chosen properties proposed by different authors are: $\log P^0$ [8], $a(\gamma_L^d)^{1/2}$ [7], boiling temperatures T_b [9], molecular refraction P_D [10], polarizability function [11], etc. More recently, a new topology index, χ_T , is defined for this application [12–14].

The chosen polar probes for the evaluation of the acid or basic character of the solid stationary phase are volatile molecules like: benzene, chloroform, acetone, ethyl acetate, diethyl ether, methylene chloride, tetrahydrofuran etc. Their electronic donor and acceptor character is found in the literature [15] as DN values and AN values. DN values, measure the energy of a co-ordinate bond between a donor atom and the Sb of SbCl₅, its value is expressed in kcal/mol (1 cal=4.184 J). AN is derived from relative ³¹P nuclear magnetic resonance (NMR) chemical shifts in Et₃PO, when dissolved in the acid species being evaluated, and is a dimensionless number. Riddle, Jr. and Fowkes [16], made corrections of Gutmann's original AN 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 [17], through the DN value of Et₃PO (the AN reference molecule) that is 40 kcal/mol. DN values can be recalculated in a dimensionless scale, or AN values in kcal/mol.

The acid–base interaction, in most papers, and also in this one, use the expression

$$Isp = (K_{a_s})DN_{probe} + (K_{b_s})AN_{probe} \quad (8)$$

where K_{a_s} and K_{b_s} are related to the acid or basic character of the solid stationary phase. These constants can be obtained plotting Isp/AN of each polar probe, versus DN/AN. The slope being K_{a_s} , and K_{b_s} the intercept.

Different methods give different results, but all of them, allow comparison of the character of the specific component of the surface energy, from one solid stationary phase to other. The units found in the literature are usually given in Isp units (kJ/mol), or in arbitrary energy units.

In this paper a new approach is proposed to split the total interaction energy of each polar probe and the estimation of the specific interaction.

2.4. New method proposed

It is well known that Kóvats indices of any compound are useful in analytical work because their values are independent of many variables like flow-rate, column size, dead volume, % stationary phase,

contact area, etc. Their value, I_x , is only dependent on the analyte characteristics, the characteristics of the stationary phase, and the temperature [18].

The difference between the Kóvats index, I_x , of a polar probe on column x , and the Kóvats index, I_{REF} , of the same probe on a non-polar reference column, it is a measure of the polar character of the column x , and reflects the specific interaction of that particular probe with column x . This is the shift of Kóvats index, ΔI , and it is given by

$$\Delta I = I_x - I_{REF} \quad (9)$$

In this paper we have used solid polyethylene (PE) as non-polar reference stationary phase. Therefore, the chosen property is the Kóvats index of the polar probe in PE, I_{PE} , which we measure in the laboratory at different temperatures.

In order to check if different mechanisms of retention would affect the results of the method, we make the same calculations taking as reference, the Kóvats index, I_{APZ} , in a column of Apiezon L. This is a liquid, quite non-polar stationary phase, and the retention of a probe, is the result of gas–liquid partitioning and adsorption phenomena. The I_{APZ}^{70} values used, are those found in the literature, [18], determined at 70°C.

3. Experimental

The instrument used was a Perkin-Elmer Autosystem with FID system with the lowest attenuation, in the limit of detection. The amount of probes injected was 0.01 to 0.05 μl of gas, taken from the headspace of the vessels, to be sure of working at

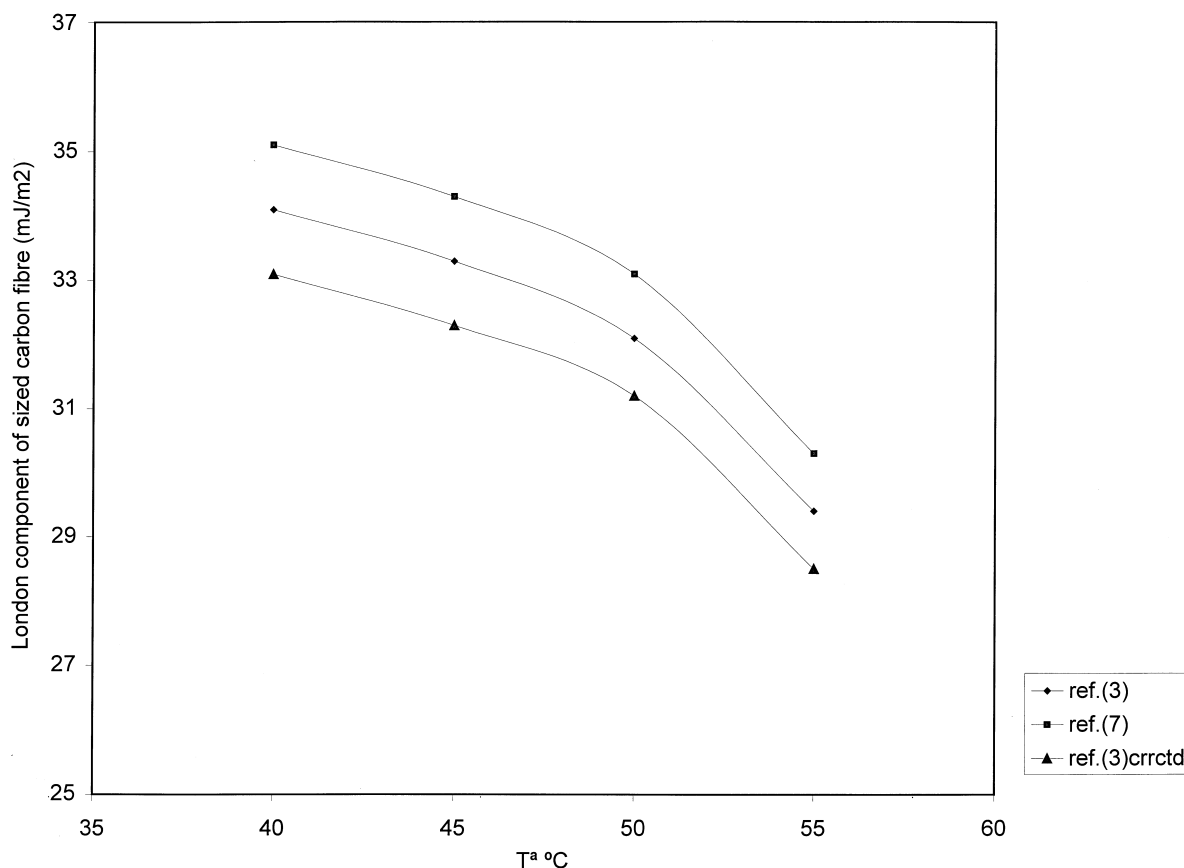


Fig. 1. London component of a sized carbon fibre at four temperatures.

Table 1
London component of surface energies of the samples in mJ/m^2

Sample	Dorris and Gray [3]	Schultz et al. [7]	Dorris and Gray (corrected)
(1) c fib sz 5131	29	30	28
(2) c fib sz 5331	30	31	29
(3) c fib not szd	39	41	38
(4) c fib szd	32	33	31
(5) res LB-64 lqd	33	34	32
(6) res 8552 cured	35	36	34
(7) res3501-6 cured	30	30	29
(8) PP+tlcm+EPDM	95	98	92
(9) PP+tlcm	90	93	87
(10) SP 1000	19	20	19

infinite dilution. The carrier gas was helium and the flow-rates were in the range of 3 to 30 ml/min for each solid stationary phase studied.

Dead retention time t_M was calculated mathemati-

cally by fitting, through progressive approximation, of parameters A , B and C , the retention times of the series of n -alkanes to an exponential equation [19] of the type

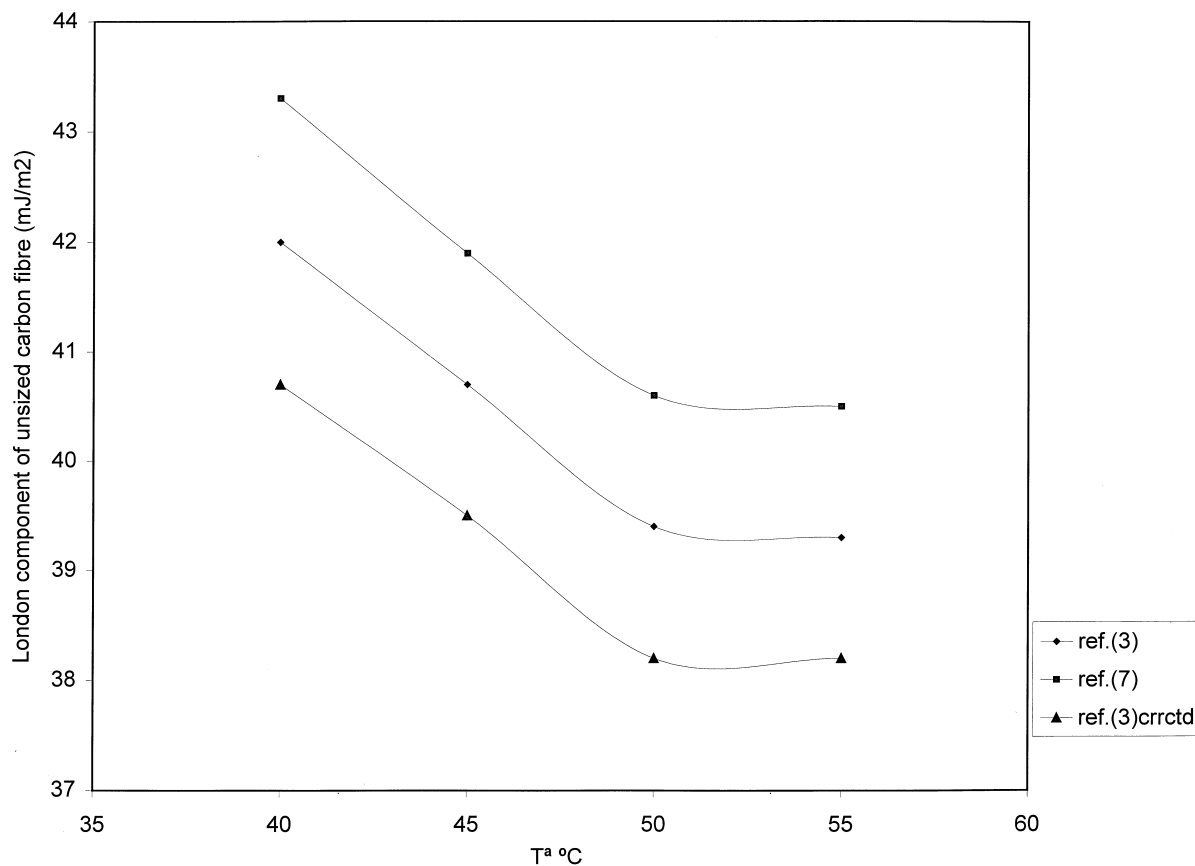


Fig. 2. London component of an unsized carbon fibre at four temperatures.

Table 2
Specific interaction of chloroform with samples, in kJ/mol

Sample	Chosen reference property						
	Log P^0 method	$a(\gamma_L^D)^{1/2}$ method	P_D method	Polariz method	I_{PE} method	I_{APZ} method	χ_T method
1	5.9	5.4	9.9	8.6	5.3	5.3	12.1
2	6.1	5.6	10.1	8.8	5.5	5.4	12.4
3	1.6	1.0	6.2	4.7	0.9	0.9	8.8
4	3.4	2.9	7.6	6.2	2.8	2.8	9.9
5	5.1	4.5	9.2	7.9	4.4	4.4	4.4
6	2.6	2.1	6.9	5.5	2.0	1.9	1.9
7	1.6	1.1	5.5	4.2	1.0	0.9	0.9
8	-0.2	-1.2	6.9	4.5	-1.3	-1.4	-1.4
9	1.5	0.6	8.4	6.1	0.4	0.4	0.4
10	8.5	8.0	11.6	10.5	7.7	7.9	7.9

$$t_R = A + \exp(B + Cn) \quad (10)$$

where t_R is the time of elution, and n is the number of carbon atoms in the molecule. The value t_M is calculated through Eq. (10) for $n=0$.

3.1. Materials

Carbon fibres: sample 1 is Tenax HTA with sizing 5131, sample 2 is Tenax HTA with sizing 5331, sample 3 is Hexcel AS4-12K, sample 4 is Hexcel AS4-G-3K.

Resins: sample 5 is Bakelite LB-64, liquid, sample 6 is Hexcel 8552, cured, sample 7 is Hexcel 3501-6, cured.

Polypropylenes: sample 8 is PP with talcum and EPDM, sample 9 is PP with talcum.

GC column: sample 10 is SP 1000 10% on Supelcoport 80–100 mesh.

All materials were introduced in PTFE tubing of 1/4 in. or 1/8 in. O.D. (1 in.=2.54 cm). Resins where embedded on glass beads, dried or cured inside the tubing. V_R are corrected retention volumes, calculated through

$$V_R = jF(T_r/T_a)(t_R - t_M) \quad (11)$$

where j is the James Martin coefficient, F is the carrier gas flow-rate measured at the column outlet at ambient pressure, and temperature (T_a), T_r is the reference temperature taken for all measurements, (25°C), t_R is the elution time and t_M is the elution time of a hypothetical unretained probe, calculated with Eq. (10) for $n=0$.

Table 3
Specific interaction of tetrahydrofuran with samples, in kJ/mol

Sample	Chosen reference property						
	Log P^0 method	$a(\gamma_L^D)^{1/2}$ method	P_D method	Polariz method	I_{PE} method	I_{APZ} method	χ_T method
1	5.9	6.4	11.0	11.0	5.4	5.5	8.8
2	5.7	6.2	10.9	10.9	5.2	5.3	8.6
3	3.5	4.1	9.4	9.4	2.9	3.0	6.8
4	4.5	5.1	9.8	9.9	4.0	4.1	7.5
5	5.0	5.6	10.4	10.4	4.5	4.6	8.0
6	4.0	4.6	9.6	9.6	3.5	3.6	7.1
7	4.4	4.9	9.5	9.5	3.9	4.0	7.3
8	0.8	1.8	10.0	10.0	-0.1	0.1	5.9
9	1.2	2.1	10.1	10.1	0.3	0.5	6.2
10	5.7	6.1	9.8	9.8	5.1	5.4	8.0

Table 4
Specific interaction of benzene with samples, in kJ/mol

Sample	Chosen reference property						
	Log P^0 method	$a(\gamma_L^D)^{1/2}$ method	P_D method	Polariz method	I_{PE} method	I_{APZ} method	χ_T method
1	4.6	4.7	7.7	7.1	4.0	3.7	7.2
2	4.7	4.7	7.8	7.1	4.1	3.7	7.3
3	0.5	0.5	4.0	3.3	-0.2	-0.7	3.4
4	2.1	2.1	5.3	4.6	1.5	1.1	4.8
5	4.0	4.1	7.3	6.6	3.4	3.0	6.7
6	1.0	1.0	4.3	3.6	0.3	-0.1	3.8
7	0.5	0.5	3.6	2.9	-0.1	-0.5	3.0
8	1.6	1.6	7.1	5.9	0.5	-0.2	6.2
9	1.5	1.5	6.9	5.7	0.4	-0.2	6.0
10	6.3	6.0	8.4	7.9	5.3	5.2	8.0

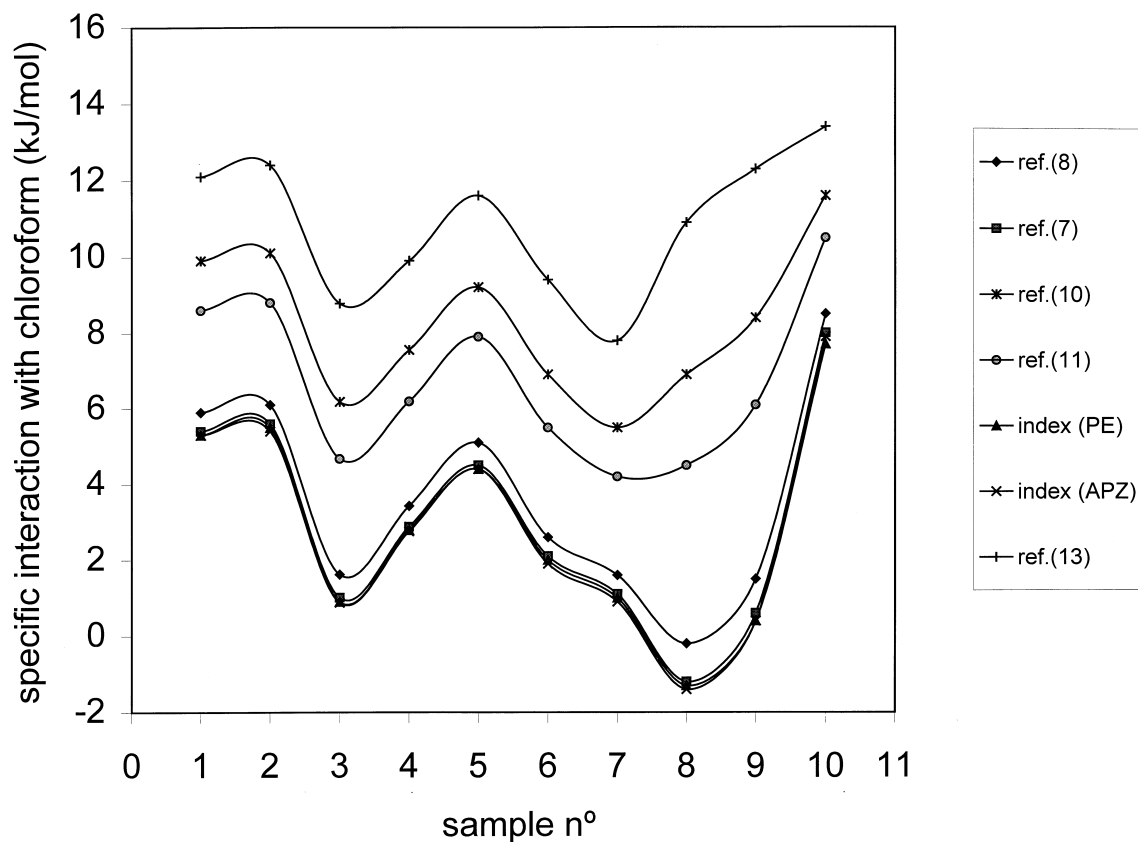


Fig. 3. Specific interaction of chloroform with 10 samples by different methods in kJ/mol.

4. Results and discussion

4.1. London component of samples studied

The London components of the free surface energy of the samples are included in Table 1.

The results obtained by any of the three methods rely on the areas of *n*-alkanes chosen. We have used the areas of Ref. [6], the same accepted by other authors.

In Figs. 1 and 2, the values of the London component of the surface of two carbon fibres, are given, obtained with the three methods at different temperatures. One fibre with and the other without sizing on the surface.

4.2. Specific interactions of polar probes. Comparison of methods

The specific interactions of three polar probes, chosen as examples, among the set of probes used for the determination of acid and basic character of the solid stationary phase, are given:

In Tables 2, 3 and 4, the specific interaction of three polar probes, an acid (chloroform), a predominantly base (tetrahydrofuran), and an aromatic ring (benzene), respectively, are given. These values, are obtained by different methods described in the literature, and with the new proposed method, for the 10 samples studied. Results are given in kJ/mol.

The graphic plots of these values are very informative. They are displayed in Figs. 3, 4 and 5.

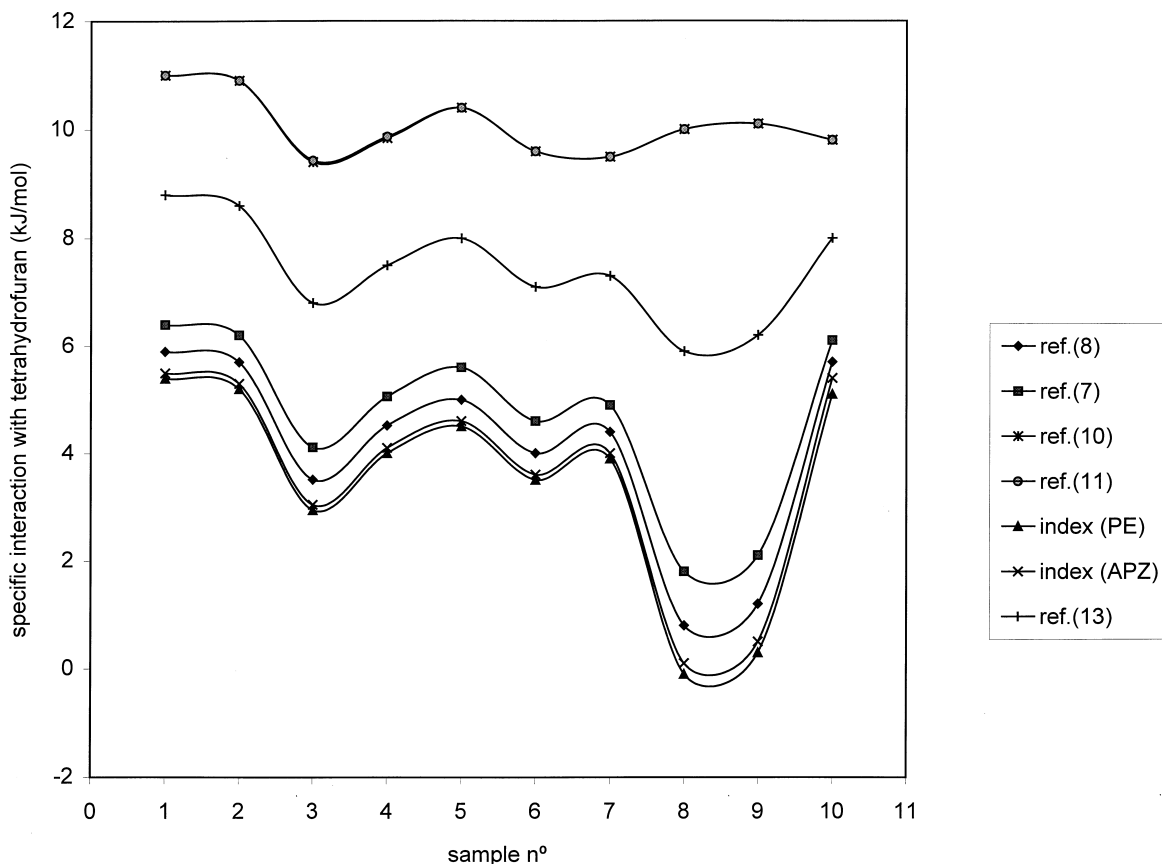


Fig. 4. Specific interaction of tetrahydrofuran with 10 samples by different methods in kJ/mol.

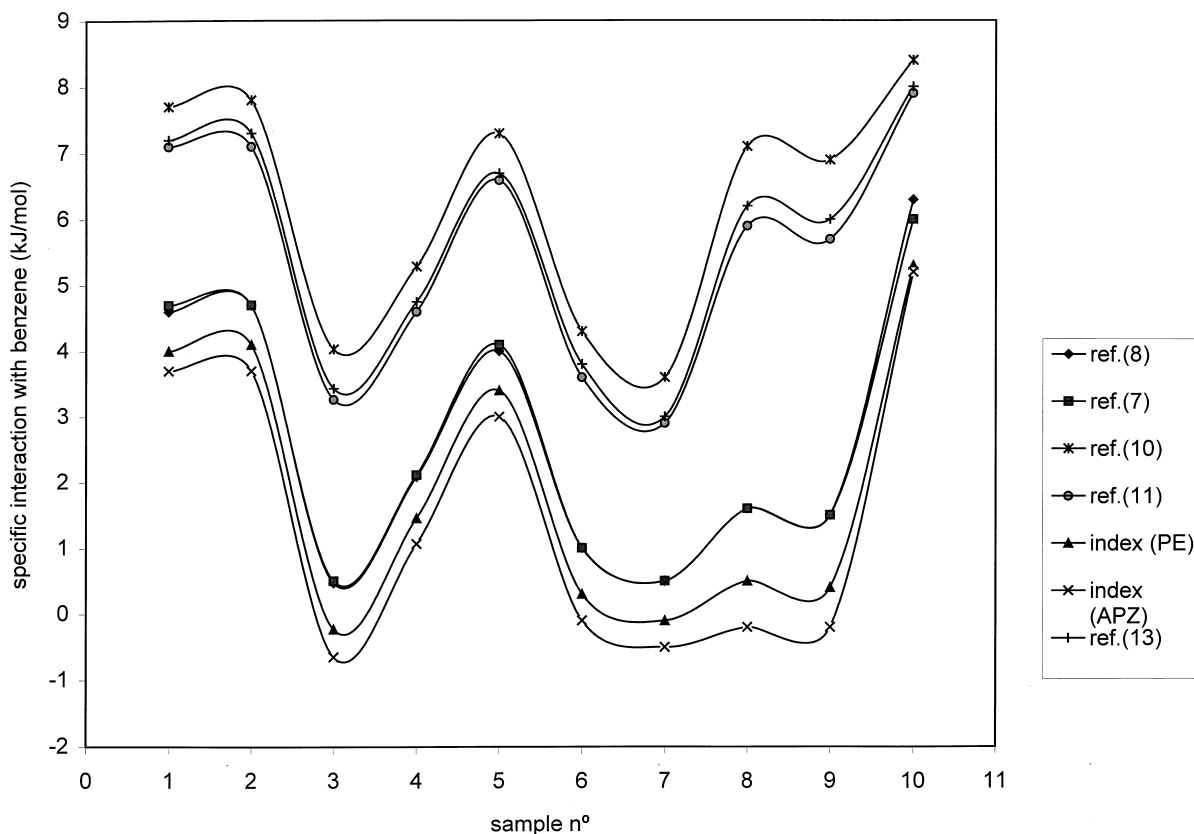


Fig. 5. Specific interaction of benzene with 10 samples by different methods in kJ/mol.

(1) There is a good agreement between the results obtained with the Kóvats index methods I_{PE} and I_{APZ}^{70} , and fairly good correlation with the methods described by Schultz et al. and St. Flour and Papirer.

(2) Those methods that use as reference a parameter of polar probes in close relation with the polarizability of the molecules, like both methods of Donnet et al., and the topology index method, the specific interaction of the polar probes is very high, if compared with the interactions obtained with other methods.

(3) The similar results obtained in our proposed method when using as a solid non-polar PE column as a reference column, or when using a liquid non-polar stationary phase like Apiezon L, leads us to the conclusion, that the Kóvats index method, is not affected by the mechanism of retention, and there-

fore, can be applied, not only to solid samples, but also to liquid samples like uncured resins or low-molecular-mass polymers.

4.3. Critical discussion of the various methods

The *chosen property* to divide the total adsorption energy in the dispersive and specific components is the key that distinguishes different methods.

(a) T_b is, in our opinion, a doubtful criterion for finding the *hypothetical equivalent hydrocarbon* with the same dispersive interaction than the polar probe.

(b) $\log P^0$. We have the same doubt as above, with this parameter. Data are easily available at any working temperature, but near the boiling point of the probes, enormous deviations are to be expected with minor changes in oven temperature, as the

Table 5
Indices (equivalent carbon number of linear alkane) for polar probes

Polar probes	χ_T	$I_{PE}^{70}/100$	$I_{APZ}^{70}/100$
Benzene	5.39	6.71	6.90
Chloroform	3.21	6.03	6.13
Acetone	3.61	4.53	4.47
Ethyl acetate	5.44	5.75	5.57
Diethyl ether	4.77	4.90	4.76
Tetrahydrofuran	4.79	6.14	6.18
Methylene chloride		5.41	5.13
Carbon tetrachloride		6.30	6.71
1-Hexene		5.84	5.87

growth rate of vapour pressure with temperature, is exponential.

(c) P_D and polarizability. Both give concordant results. We consider that with these parameters, an overestimation of the polar interaction occurs. Data

of molecular refractivity are easily available but not at any temperature. Data of polarizability are more difficult to find for polar probes, and also there is no information on the variation of its value with temperature.

(d) $a(\gamma_L^D)$. Surface energy values are function of the temperature. Only data at fixed temperatures are given. Data found in the literature are not always in agreement. Besides there is the problem in the areas, already discussed in other papers [20].

(e) Topology index, χ_T . It is an interesting approach. By definition, χ_T , is an estimation of the London interaction capacity of a probe, and is an extension of Wiener's index, for molecules containing heteroatoms, considering bond lengths, number of electrons of atoms etc. According to Ref. [13], χ_T is constant with temperature. The evaluation of specific interactions is calculated through $\Delta\chi_T$, which

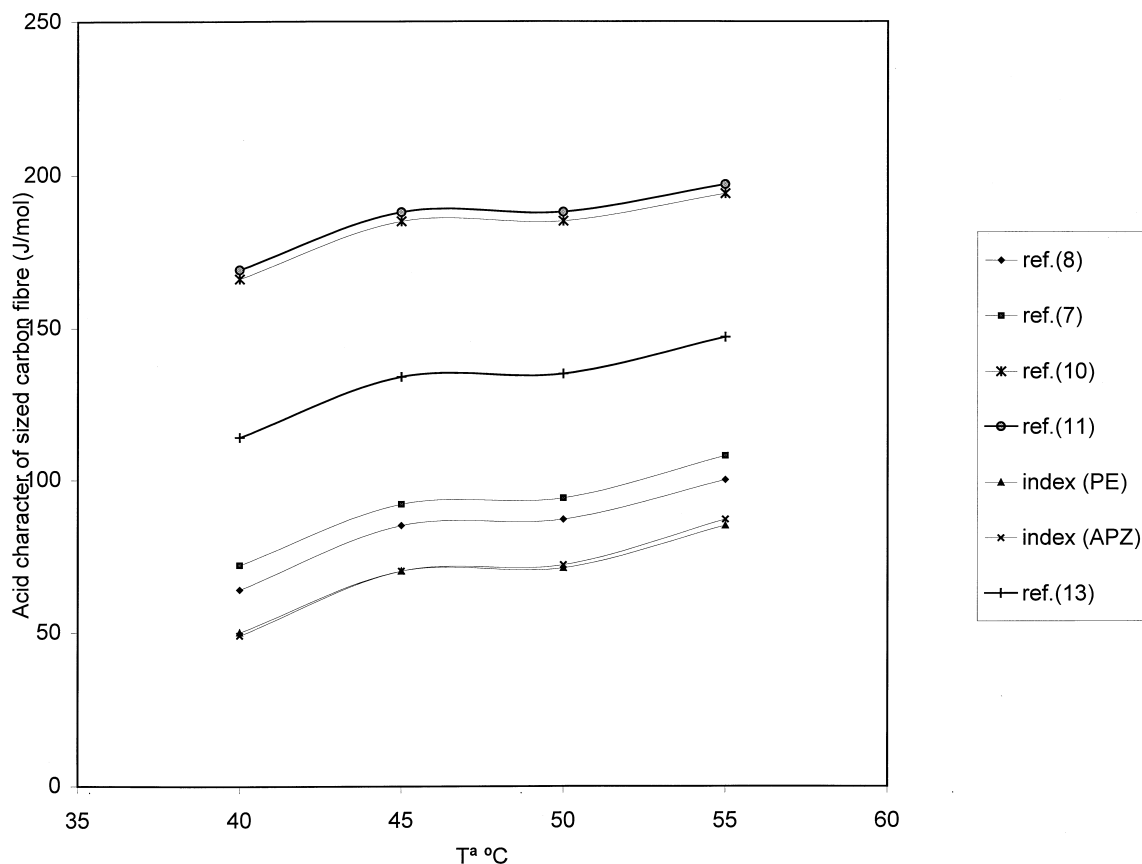


Fig. 6. Acid character of a sized carbon fibre at four temperatures, in kJ/mol. Different methods.

is similar to the shift of Kóvats index that we propose. The reference values are, nevertheless, quite different, therefore different results should be expected when comparing both methods. In Table 5 there is a comparative view of topology indexes, χ_T , I_{PE}^{70} and I_{APZ}^{70} .

(f) I_{PE} and I_{APZ} have many advantages. (i) They are easily determined. (ii) They are temperature dependent, but the variation is not great. It is easy to obtain a curve of $I_{PE}f(T^a)$, to apply the exact index at the working temperature, which may be very different when studying different materials. (iii) They can be applied to liquid or solid samples as long as they can be properly introduced in a GC column. (iv) It is possible to compare very similar materials quite accurately by using one of them as reference column and observing the shifts of Kóvats index. (v) The shifts ΔI_{PE} or ΔI_{APZ}^{70} , which measure the polarity of

the stationary phase, are given in number of $(-\text{CH}_2-)$ groups, and the adsorption energy of a $(-\text{CH}_2-)$ group, in the case column, has a value, obtained through the plot of $-\Delta G_A$ versus number of carbon atoms of the series of n -alkanes. That means a direct connection of the London component of the surface energy, obtained when injecting n -alkanes, and the specific component of the surface, explored by injecting polar probes.

4.4. Acid and basic character of carbon fibres at different temperatures

In this paper I_{PE} , and I_{APZ}^{70} have been used in spite of knowing that there is a slight variation of I_{APZ} value with the temperature. Figs. 6–9 show, the acid character (K_A), and basic character (K_B), of a carbon fibre, with and without sizing, at four different

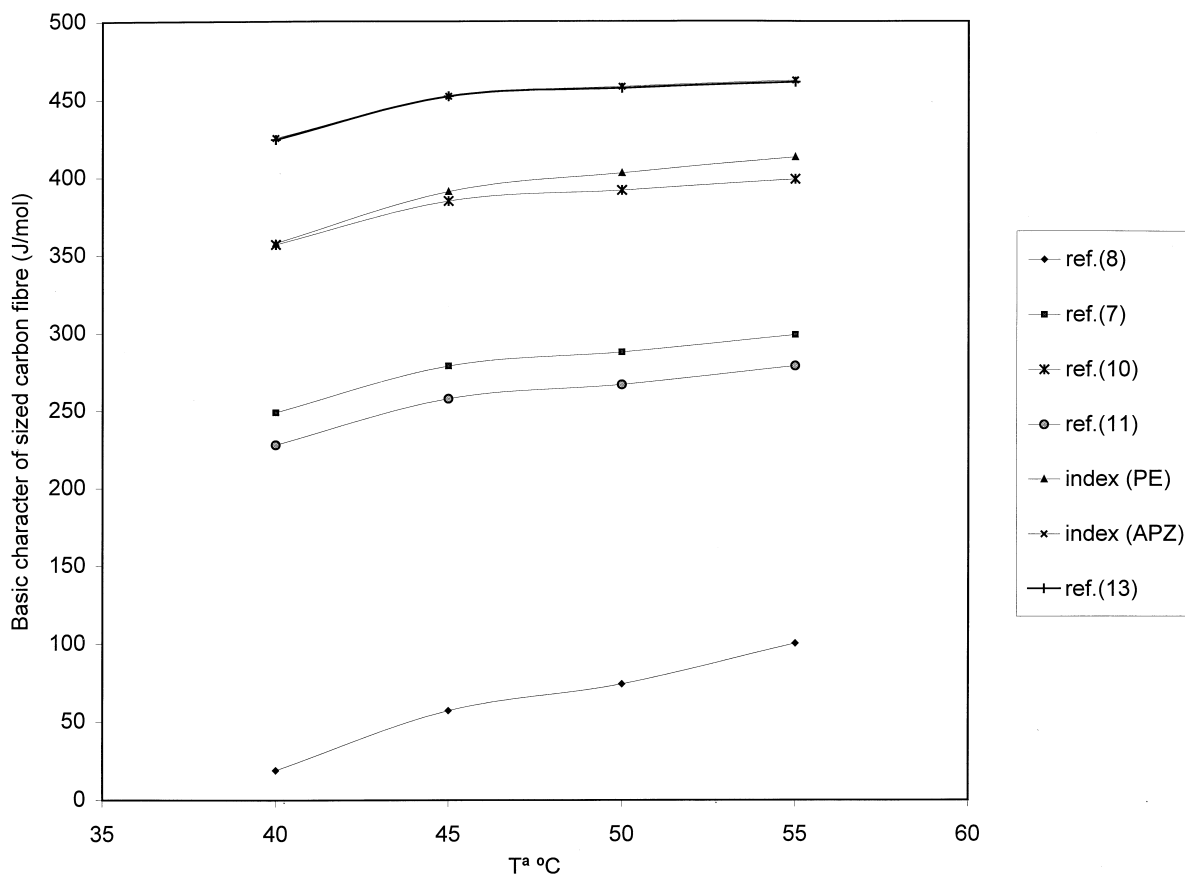


Fig. 7. Basic character of a sized carbon fibre at four temperatures, in kJ/mol. Different methods.

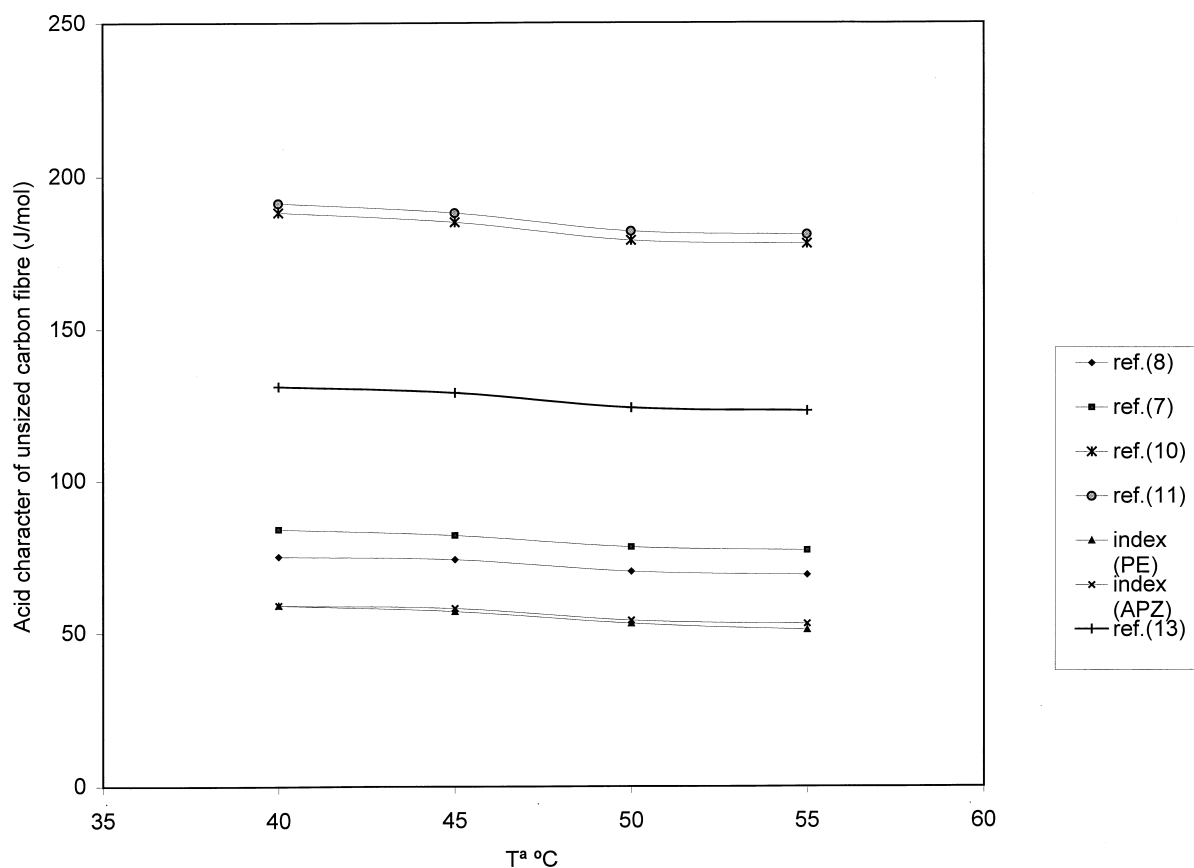


Fig. 8. Acid character of an unsized carbon fibre at four temperatures, in kJ/mol. Different methods.

temperatures, by the methods of St. Flour and Papirer [8], Schultz et al. [7], Dong et al. [10], Donnet et al. [11], Brendlé and Papirer [13], and the proposed method of shift of Kóvats indices, using I_{PE}^{70} and I_{APZ}^{70} as references.

AN and DN values used, are those given in the literature [21,22], corrections are made according to Ref. [17], to normalise scales, in dimensionless numbers. K_A and K_B obtained are given in J/mol.

Acid and basic character of the stationary phase, can be converted in energy per surface units (mJ/m²) by measuring the work of adsorption of polar probes in CH₂ adsorption units. The proposed method and the topology index method, give this parameter. All other methods, need to calculate this parameter with the slope of the respective *n*-alkane line. The value of one CH₂ adsorption, is calculated through the plot of $-\Delta G_A$ versus number of carbon atoms in *n*-alkane molecules. This value can be obtained in

energy units per mol of CH₂ or in energy units per surface area units if we accept an interaction area of CH₂, such as those given in Ref. [6].

The polar probes injected are: chloroform, acetone, ethyl acetate, tetrahydrofuran and methylene chloride for the determination of the acid–base character of the problem. Lines are obtained ($r^2 > 0.98$), when plotting I_{sp}/AN versus DN/AN . The slope gives us K_A of the sample, and the intercept K_B .

5. Conclusions

(1) A method is proposed for evaluation of specific interactions of polar probes by IGC. Any volatile polar compound can be used as probe and the shift of Kóvats index can be easily obtained for

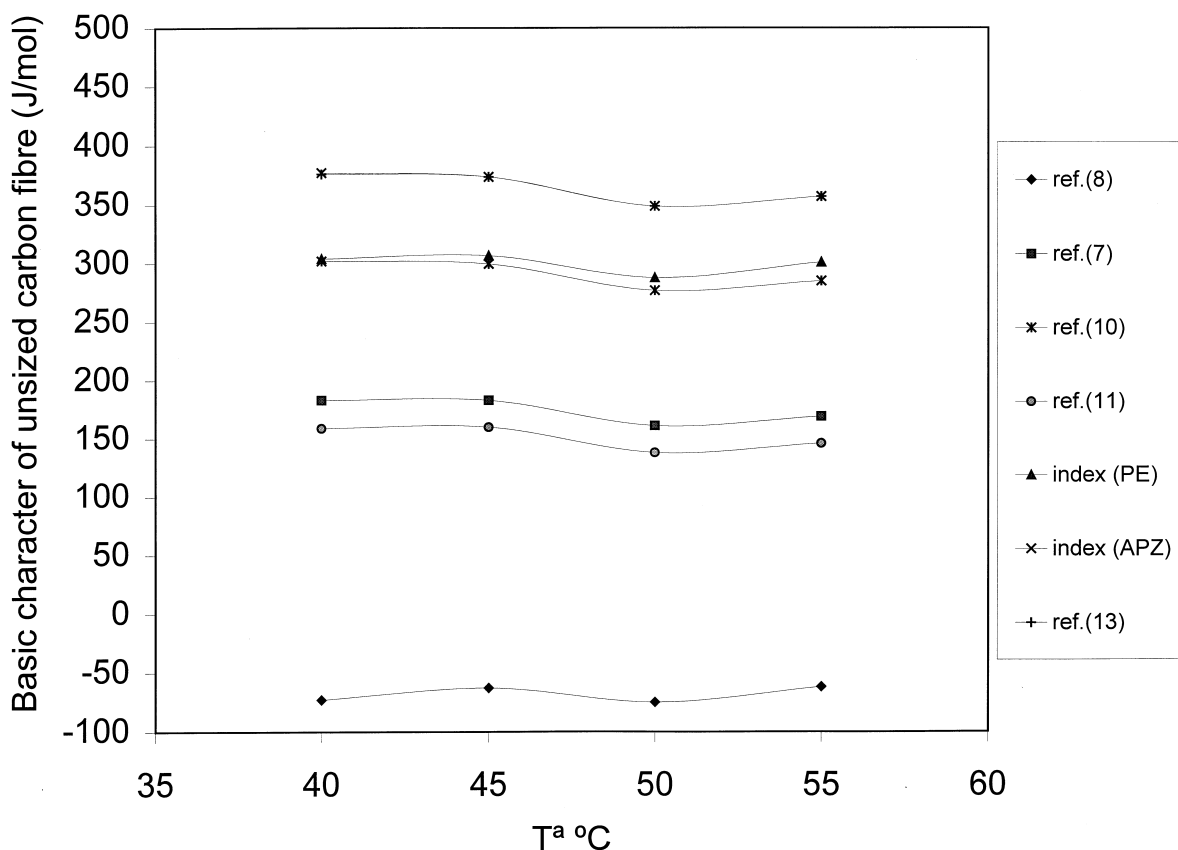


Fig. 9. Basic character of an unsized carbon fibre at four temperatures, in kJ/mol. Different methods.

any compound using as reference any convenient column.

(2) The results obtained with this method are in good agreement with those obtained by Schultz et al. and in fairly good agreement with those obtained by St. Flour and Papirer. The new method has no problematic search of reliable data of surface free energies and contact areas of the polar probe molecules.

(3) I_{PE} values, here proposed as *chosen property* for splitting the adsorption energy of the probes and the solid surface, can be obtained at any working temperature, avoiding the errors caused by ignoring the variation of the property with temperature.

(4) The units of specific interaction measured by the proposed method are “*number of CH₂ groups*”, or which is the same, the *energy of interaction of those number of CH₂ groups with that particular stationary phase*. This means a direct connection

between the dispersive component of the surface energy obtained through the slope of the *n*-alkane line, and the acid and basic character of the surface.

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