New approach to characterise physicochemical properties of solid substrates by inverse gas chromatography at infinite dilution I. Some new methods to determine the surface areas of some molecules adsorbed on solid surfaces

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Abstract

This study was divided into three different parts that tried to give a new contribution to determine and quantify more precisely the superficial properties of solid substrates (polymers and/or oxides) obtained by inverse gas chromatography (IGC) at infinite dilution. It criticised certain of the classical methods and relationships used to determine some physico-chemical properties of a solid and gave new methods and equations that can be more precise and more realistic. Part I developed some new methods to determine the surface areas of some molecules adsorbed on solids. A theoretical calculation of surface areas of molecules adsorbed on solid substrates was proposed by using some theoretical models. Two new methods to determine the surface areas of polar molecules were developed. The first one consists of the determination of surface areas by coupling two classical methods, the dynamic contact angle and IGC techniques. The second new and general method, using the IGC technique, assumes that the specific interactions between a polar molecule and a solid proposed by Papirer and Schultz are the same. A new equation was obtained to determine the surface areas of polar molecules.
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1. Introduction

The determination of molecular areas of *n*-alkanes and polar molecules adsorbed onto solid surfaces (metals, oxides or polymers) is of vital importance in studying the fundamental properties of surfaces and materials that are related closely to adsorption, wetting, adhesion, and other surface and interface phenomena [1,2]. Indeed, in the inverse gas chromatography (IGC), the *n*-alkanes are used as probes to determine the dispersive component of surface energy γ_s^d and serve to estimate the specific component of surface energy of particles and fibres which are difficult to measure by other methods, like contact angle [3,4]. Another method is used to determine the specific interactions of a solid ex-

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changed with some polar organic molecules using the notion of the vapour pressure of the probes [5–7]. However, even if this last method does not use the values of the surface areas a of adsorbed molecules, then the determination of the dispersive surface energy component γ_s^d of the solid necessitates the precise knowledge of the surface areas of n-alkanes adsorbed on the solid substrate.

IGC at infinite dilution [8,9] is used to characterise the surface characteristics of various oxides and polymers. 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, in the absence of interactions between the probe molecules themselves.

The net retention volume V_n was calculated from:

$$V_n = j \, D_c \, (t_R - t_0) \tag{1}$$

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 [9]. D_c and j are respectively given by the following expressions:

$$D_c = j D_m \cdot \frac{T_c}{T_a} \cdot \frac{\eta(T_c)}{\eta(T_a)} \tag{2}$$

with

$$j = \frac{3}{2} \cdot \frac{\left(\dfrac{\Delta P + P_0}{P_0}\right)^2 - 1}{\left(\dfrac{\Delta P + P_0}{P_0}\right)^3 - 1} \tag{3}$$

where D_m is the measured flow-rate, T_c the column temperature, T_a the room temperature, $\eta(T)$ the viscosity gas, P_0 the atmospheric pressure and ΔP the pressure variation.

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

$$\Delta G^0 = RT \ln V_n + C \tag{4}$$

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 ad-

sorption corresponding to dispersive interactions ΔG^d only.

We propose in this study to give some new methods to determine the surface areas of molecules adsorbed on a solid, like polytetrafluoroethylene (PTFE), ZnO or MgO, by using principally the IGC technique. Section 2 will give the details of the methods consisting of the determination of the specific interactions and γ_s^d of the solid and will display the various models allowing to obtain the surface areas of polar molecules. Section 3 will give the experimental details and results, and will compare our results to those obtained by other models or methods. Section 4 will be devoted to the conclusions.

2. Theory

2.1. Methods of IGC

2.1.1. Determination of specific interactions

The method used to obtain specific enthalpy of interaction between a probe and a solid is that developed by Saint Flour and Papirer [5–7] who 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, whatever the nature of the solid substrates:

$$RT \ln V_n = A \ln P_0 + B \tag{5}$$

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

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

$$\Delta G^0 = \Delta G^d + \Delta G^{sp} \tag{6}$$

where ΔG^{sp} refers to specific interactions as shown in Fig. 1.

The specific interactions of the polar molecules with the solid substrates can be used to determine the acidic and basic constants using the donor (DN) and acceptor (AN) numbers of polar molecules.
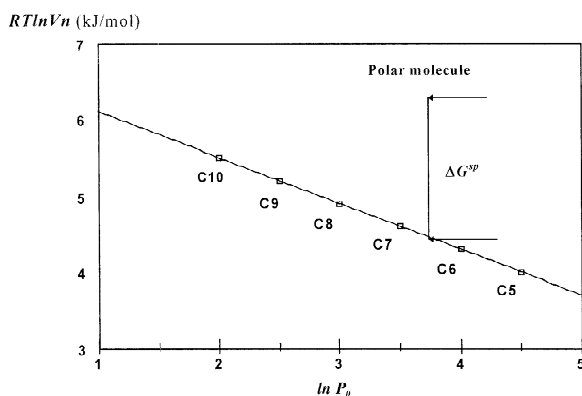
Fig. 1. Variation of the logarithm of the retention volume of *n*-alkanes versus the logarithm of the vapour pressure.

2.1.2. Determination of the dispersive component of the surface energy of solids γ_s^d

When non-polar solids, such as *n*-alkanes, are used, ΔG^0 can be related to the London interactions by using the well-known relationship of Fowkes [10] expressing the geometric mean of the dispersive components (exponent 'd') of the surface energy of the probe γ_1^d and the solid γ_s^d:

$$\Delta G^0 = \Delta G^d = 2\mathcal{N}a\sqrt{\gamma_1^d \gamma_s^d} \qquad (7)$$

where $\mathcal{N}$ is Avogadro's number and a the surface area of one adsorbed molecule of the probe.

By plotting $RT \ln V_n$ as a function of $2\mathcal{N}a\sqrt{\gamma_1^d}$ of *n*-alkanes (Fig. 2), we can deduce, from the slope of the straight line, the value of dispersive component of the surface energy of the solid [11].
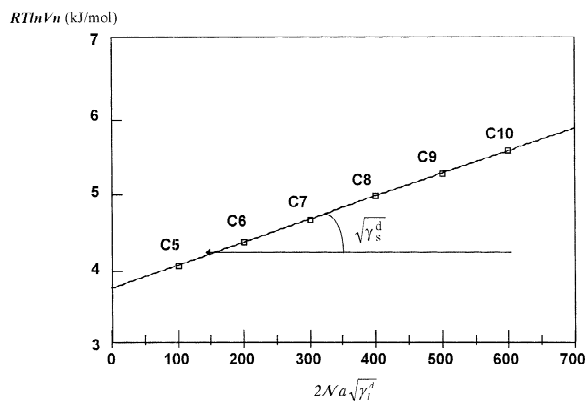

Fig. 2. Variation of the logarithm of the net retention volume of *n*-alkanes versus $2\mathcal{N}a\sqrt{\gamma_1^d}$ of probes.

However, the surface area a of a molecule adsorbed on a solid substrate is not known with a good accuracy, hence we will give in the next section some new methods to determine more precisely the surface areas of some polar molecules adsorbed on non-polar or polar solid surfaces.

2.2. Theoretical calculation of the surface areas of molecules

2.2.1. Some models to calculate the molecular areas of n-alkanes

Various theoretical models can be used to obtain the molecular areas of *n*-alkanes:
1. Van der Waals (VDW) model;
2. Redlich–Kwong (R–K) equation;
3. projection or geometric model;
4. cylindrical molecular model (from density data);
5. spherical model (from density data).

Other results were experimentally obtained by Kiselev and BET methods.

2.2.1.1. Van der Waals and Redlich–Kwong equations

From the critical co-ordinate data of *n*-alkanes, we also calculated the surface areas of these molecules, using VDW or R–K equations [12–27] and compared them with those obtained from the molecular projection. Results are presented in Table 1.

2.2.1.2. Models using the liquid density

Molecular area can be calculated by using the liquid density and admitting a certain form and position of the adsorbed molecule. Two possibilities can be distinguished: spherical or cylindrical models of molecules.

(i) By supposing that the linear long-chain hydrocarbon molecule is like a cylinder having a radius r and length L, Donnet et al. [28] calculated the projected area σ_a of the cylindrical molecule by using the liquid density, the molar mass of the *n*-alkanes and the dimensions r and L of the cylinder.

(ii) By using the spherical model of the molecule, the liquid density and the molar mass of the *n*-alkanes

Table 1 gives the surface areas of some *n*-alkane molecules obtained by Donnet et al. [28]. We ob-

Table 1
Surface areas of the different molecules (in $\mathring{A}^2$) obtained from VDW and R–K equations, the geometric projection model (molecules are assumed to be adsorbed in parallel position to the solid surface), compared to those obtained by Kiselev and co-workers [29–34] and Donnet et al. [28] using both spherical and cylindrical models

| Molecules | Models or equations used to determine the surface areas of *n*-alkanes (in $\mathring{A}^2$) | | | | | |
	VDW equation	R–K equation	Geometric model	Kiselev results	Cylindrical model	Spherical model
CH_4	20.8	16.3	7.4	–	–	–
C_2H_6	27.1	21.2	9.5	–	–	–
C_3H_8	32.7	25.6	17.3	–	–	–
C_4H_{10}	41.9	32.8	25.1	–	–	–
C_5H_{12}	47.0	36.8	32.9	45	39.3	36.4
C_6H_{14}	52.8	41.3	40.7	51.5	45.5	39.6
C_7H_{16}	59.2	46.4	48.5	57	51.8	42.7
C_8H_{18}	64.9	50.8	56.3	63	58.1	45.7
C_9H_{20}	69.6	54.5	64.0	69	64.4	48.7
$C_{10}H_{22}$	74.4	58.2	71.8	75	70.7	51.7

served that the spherical model estimates by default the surface areas of *n*-alkanes relative to those obtained by the cylindrical model.

2.2.2. Surface areas of polar molecules

In this section, we calculated radii r_d of certain polar molecules by using their liquid densities admitting a spherical geometry. Table 2 gives these values including radii of gyration r_g [35] of the different molecules as well as those r_q obtained by quantum considerations [36]. In Part 3, one will also give variations of the mean molecular radii of the polar molecules, obtained experimentally as a function of the temperature.

In Table 3, we give the surface areas of some polar molecules adsorbed on graphitised carbon black or on PTFE powder [37], compared to those respectively obtained by Synder [8], BET [38], spherical model and geometric model.

3. Experimental

3.1. Chemicals

The following materials were used: polytetrafluoroethylene (PTFE) fibres from Goodfellow (Huntingdon, UK), exhibiting a diameter equal to 200 µm; zinc oxide powder obtained from Sigma–Aldrich (St. Quentin Fallavier, France) of high purity

Table 2
Values of the radii of polar molecules obtained from the liquid density, r_d, quantum data r_q and from the gyration radii r_g

Molecule	Radius calculated from the liquid density at 20 °C r_d (in $\mathring{A}$)	Radius calculated from quantum data r_q (in $\mathring{A}$)	Gyration radius r_g (in $\mathring{A}$)
CCl_4	3.20	2.974	3.458
$CHCl_3$	3.01	2.695	3.178
CH_2Cl_2	2.79	2.449	2.342
CH_3CN	2.61	–	1.821
Ethanol	2.71	2.265	2.250
Diethyl ether	3.28	2.839	3.140
Acetone	2.92	2.300	2.740
Ethyl acetate	3.22	2.603	3.348
C_6H_6	3.17	2.675	3.004
Toluene	3.31	–	3.443

Table 3
Values of surface areas of some polar probes adsorbed on solids given in literature [8,37,38]

Molecule	Surface areas (in $\mathring{A}^2$)					
	Adsorbed at 47.4 °C [37] on non-polar substrates:		Other values of surface areas obtained by:			
	PTFE powder	Graphitised carbon black	Synder [8]	BET [38]	Spherical model	Geometric model
CCl_4	46	35	43	37	32	20
$CHCl_3$	44	21	43	32	29	18
CH_2Cl_2	39	23	35	27	25	14
CH_3CN	47	–	85	28	21	20
Ethanol	50	–	68	–	23	21
Diethyl ether	55	42	38	25	34	34
Acetone	55	31	36	25	27	30
Ethyl acetate	60	41	48	28	33	33
C_6H_6	47	41	51	40	31	36
Toluene	–	–	–	–	34	43

(greater than 99%), with particle sizes comprised between 100 and 200 μm, specific surface area equal to 4 m^2/g; magnesium oxide powder from Cerac-Neyco (Paris, France) with a 99.95% purity having a specific surface area equal to 2 m^2/g; model organic molecules: we used some organic polar molecules, namely, toluene, ethanol, diethyl ether, ethyl acetate, acetone, tetrahydrofuran (THF), CCl_4 $CHCl_3$, CH_2Cl_2, CH_3CN and C_6H_6, which are characterized by their donor and acceptor numbers [39,40]. We also used *n*-alkanes (C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$, etc.) as non-polar molecules; all organic molecules used in this study were purchased from Prolabo (Strasbourg, France).

3.2. Chromatographic procedure

Two principal techniques were used in this study. The first one is IGC at infinite dilution and the second technique is that of the dynamic contact angle (DCA) analyzer.

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 ionisation detector of high sensitivity. The retention data were obtained with a stainless steel column of length 30 cm and 2 mm internal diameter packed with 1.5 g of polymer powders.

In this study, we used PTFE fibres as a non-polar solid surface. The PTFE fibres (about 1.5 g) having a diameter of 200 μm were introduced in the column. Before measurements, the PTFE fibres were flushed, over a night, with helium (He) as carrier gas at a flow-rate of about 25 ml min^{-1}, at 120 °C, so as to eliminate physically adsorbed impurities. Here, 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 done by varying the temperature from 20 °C to 120 °C. The retention times obtained by this study allowed to obtain the net retention volume using Eq. (1).

The same procedure was used with the other solid substrates ZnO and MgO at 50 °C with the same experimental conditions.

On the other hand, we obtained the surface energy of the PTFE fibres at different temperatures by using a second technique, the dynamic contact angle (DCA) analyzer purchased from Cahn Instruments (Cerritos, USA). The DCA analyzer allowed in a previous study [41] measurement of the dispersive component of the suface energy of the same PTFE fibres (previously used in IGC) as a function of the temperature.

Table 4

Values of the dispersive surface energy γ_s^d of PTFE and equations of $RT \ln V_n = f(a\sqrt{\gamma_l^d})$ obtained from the previous models at 81.2 °C

Model tested at 81.2 °C	Equations giving $RT \ln V_n$ (in kJ/mol) versus $a\sqrt{\gamma_l^d}$ (a in Å^2 and γ_l^d in mJ/m^2)	Theoretical values of γ_s^d (mJ/m^2)
Redlich–Kwong	$RT \ln V_n = 2.28 + 5.43 \cdot 10^{-2} a\sqrt{\gamma_+^d}$	20.3
Geometric model	$RT \ln V_n = 5.95 + 3.22 \cdot 10^{-2} a\sqrt{\gamma_+^d}$	7.1
Van der Waals model	$RT \ln V_n = 2.30 + 4.24 \cdot 10^{-2} a\sqrt{\gamma_+^d}$	12.4
Spherical model	$RT \ln V_n = 1.11 + 6.65 \cdot 10^{-2} a\sqrt{\gamma_+^d}$	30.5
Cylindrical model	$RT \ln V_n = 4.54 + 3.73 \cdot 10^{-2} a\sqrt{\gamma_+^d}$	9.6
Kiselev results	$RT \ln V_n = 3.70 + 3.78 \cdot 10^{-2} a\sqrt{\gamma_l^d}$	9.9

Experimental value of γ_s^d of PTFE at 81.2 °C: γ_s^d (exp.) = 13.6±1 mJ/m^2

3.3. Results

3.3.1. A first method to calculate the surface areas of polar molecules

Using IGC at infinite dilution, we can correlate the net retention volume to the free energy of adsorption ΔG^0 of one molecule on a solid by Eq. (8):

$$- \Delta G^0 = - (\Delta G^d + \Delta G^{sp}) = RT \ln V_n + C \qquad (8)$$

In the case of a non-polar solid surface, $\Delta G^{sp} = 0$, the experimental values of ΔG^0 (obtained by IGC) for polar probes must be located on the straight line of ΔG^d versus $2\mathcal{N}a\sqrt{\gamma_l^d}$ corresponding to the series of n-alkanes.

This procedure will allow us to determine the surface area a of the adsorbed molecule of the polar probe, knowing the dispersive surface energy components γ_l^d of the probe and γ_s^d of the solid. PTFE fibres were used as the reference non-polar solid surface. The surface energy γ_s of this solid equal to its dispersive component γ_s^d was determined as a function of temperature, through wetting measurements using the DCA technique [41]:

$$\gamma_s^d = \gamma_s = 23.09 - 0.117\,T \qquad (9)$$

where γ_s^d is expressed in mJ/m^2 and T in °C.

The values of γ_s^d of PTFE determined by DCA at various temperatures were used as a reference to obtain the best model giving a good agreement between the experimental value (determined by DCA) and the calculated value (obtained by IGC).

The following models giving the molecular areas of n-alkanes were used and tested between 20 °C and 150 °C: cylindrical (Cyl.) and spherical (Sph.) molecular models using the liquid density model, Geometric model (Geom.), Kiselev results, VDW model and R–K model.

We used the above procedure at different temperatures and determined the various equations for all the models tested by this method. The value of the dispersive surface energy γ_s^d of PTFE obtained by every model was compared to the experimental value γ_s^d determined by IGC and DCA techniques.

As an example, we give in Table 4 the theoretical and experimental results obtained at 81.2 °C. Repeating this procedure with other temperatures, we can deduce the optimized model allowing to obtain the surface areas of polar molecules (Table 5).

From Table 5, we can deduce the surface area values of some polar molecules adsorbed on PTFE fibres at different temperatures (Table 6).

To compare our results with those obtained in the literature, we give in Table 7, the values of surface

Table 5

Optimization of the model allowing to determine the various surface areas of polar molecules for different temperatures

Optimal model	T (°C)	Equation valid for the calculation of the surface areas of polar molecules	γ_s^d (theo.) (mJ/m^2)	γ_s^d (exp.) (mJ/m^2)
Kiselev	50.9	$RT \ln V_n = -0.92 + 4.96 \cdot 10^{-2} a\sqrt{\gamma_l^d}$	17	17.1±1
cylindrical	50.9	$RT \ln V_n = 0.42 + 4.86 \cdot 10^{-2} a\sqrt{\gamma_+^d}$	16.3	17.1±1
VDW	81.2	$RT \ln V_n = 2.30 + 4.24 \cdot 10^{-2} a\sqrt{\gamma_+^d}$	12.4	13.6±1
Redlich–Kwong	120	$RT \ln V_n = 7.55 + 3.59 \cdot 10^{-2} a\sqrt{\gamma_l^d}$	8.9	9.1±1

Table 6
Surface areas of polar molecules adsorbed on PTFE versus the temperature, determined from the best model optimizing the value of the surface energy

Molecule	Experimental values (in Å^2) of surface areas of molecules adsorbed on PTFE at:			
	50.9 °C (Kiselev)	50.9 °C (Cyl.)	81.2 °C (VDW)	120 °C (R–K)
CCl_4	49±2	44±4	47±4	43±1
$CHCl_3$	45±2	41±4	37±3	28±1
CH_2Cl_2	51±2	46±4	46±4	35±1
CH_3CN	71±3	65±5	65±5	48±2
Ethanol	57±2	52±5	50±4	34±1
Diethyl ether	47±2	41±4	39±3	34±1
Acetone	61±3	55±5	54±4	39±1
Ethyl acetate	50±2	37±3	42±3	32±1
C_6H_6	54±2	49±4	50±4	44±2
Toluene	58±3	54±5	48±4	40±5

areas of certain polar molecules determined by our methods compared with Synder and BET results and those of the projection model.

Table 7 shows that the values obtained by our method are higher than those obtained by Synder, BET or the geometric model for the various molecules and at different temperatures. The value of surface area then is extremely dependent on the method used and on the nature of the solid substrates.

3.3.2. A new general method

IGC at infinite dilution is a good technique which is particularly applied to the the determination of surface properties of various solids as dispersive and

specific interactions, for example. Two methods are generally used:

(i) The first one, Papirer et al.'s approach [5–7], relates the free energy of adsorption ΔG^0 of molecules adsorbed on a solid, to the logarithm of the vapour pressure P_0 of solutes. The relationship is given by the following equation:

$$\Delta G^0 = -RT \ln V_n + C = \alpha \ln P_0 + \beta + C \qquad (10)$$

where α, β and C are constants depending on the solid and the chosen reference states. This method allows to calculate the specific interaction (Isp) between a polar molecule and a solid.

(ii) The second method is Schultz et al.'s approach which relates the same free energy of adsorption to the dispersive component γ_s^d of the surface energy, by the following relationship:

$$\Delta G^0 = 2\mathcal{N}a\sqrt{\gamma_l^d} + \Delta G^{sp} \qquad (11)$$

Supposing that the specific interactions between a polar molecule and a solid proposed by Papirer et al. (Isp) and Shultz et al. (ΔG^{sp}) are the same, we will be able to deduce, by this procedure, the surface areas of molecules adsorbed on solids.

$$Isp \text{ (probe)} = \Delta G^{sp}(\text{probe}) \qquad (12)$$

With Papirer's method and for a reference molecule (ref.) and a polar probe (probe) we have:

$$Isp(\text{probe}) - Isp(\text{ref.}) = RT \ln \left[\frac{V_n(\text{probe})}{V_n(\text{ref.})} \right]$$
$$- \alpha \ln \left[\frac{P_0(\text{probe})}{P_0(\text{ref.})} \right] \qquad (13)$$

Table 7
Surface areas of various polar molecules determined by our methods compared with Synder and BET results and those of the projection model

Molecule	Values of surface areas (in Å^2) obtained by our models compared with other results of the literature					
	50.9 °C	81.2 °C	120 °C	Projection model	BET	Synder
$CH_3CO\,CH_3$	55	54	39	18.4	25	36
CH_3CH_2OH	52	50	34	13.5	–	–
$CHCl_3$	41	37	28	18.2	35	43
C_6H_6	49	50	44	36.3	40	51
CCl_4	44	47	43	18.1	37	43
$CH_3CO_2C_2H_5$	37	42	32	32.6	25	48

Table 8
Comparison between the different methods at 50 °C

Molecule	Values of surface areas (in $\mathring{A}^2$) of polar molecules adsorbed on various obtained by our methods		
	MgO	ZnO	PTFE fibres (Cyl.)
CCl_4	49±1	49±1	44±4
$CHCl_3$	43±1	43±1	41±4
CH_2Cl_2	40±1	40±1	46±4
CH_3CN	70±2	69±2	65±5
Ethanol	61±2	60±2	52±5
Diethyl ether	49±2	49±2	41±4
Acetone	53±2	53±2	55±4
Ethyl acetate	58±2	58±2	37±3
C_6H_6	49±1	48±1	49±4
Toluene	56±1	56±1	54±5

If we apply Schultz's method [3,4], we obtain:

$$\Delta G^{sp}(\text{probe}) - \Delta G^{sp}(\text{ref.}) = RT \ln \left[\frac{V_n(\text{probe})}{V_n(\text{ref.})} \right]$$
$$- 2\mathcal{N}\sqrt{\gamma_s^d}\left\{ \left[a\sqrt{\gamma_l^d} \right](\text{probe}) - \left[a\sqrt{\gamma_l^d} \right](\text{ref.}) \right\}$$

By combining the two methods, we can calculate the areas of polar molecules by using the following equation:

$$a(\text{probe}) = a(\text{ref.})\sqrt{\frac{\gamma_l^d(\text{ref.})}{\gamma_l^d C}} + \frac{\alpha}{2\mathcal{N}\sqrt{\gamma_s^d}\sqrt{\gamma_l^d(\text{probe})}}$$
$$+ \ln \left[\frac{P_0(\text{ref.})}{P_0(\text{probe})} \right] \qquad (14)$$

By choosing chloroform as reference, we calculated, from Eq. (14), polar molecule areas adsorbed on MgO and ZnO (for example) and we compared it with other results previously obtained (Table 8).

The combination of the two methods of Schultz et al. and Papirer et al. allowed to obtain the same values of surface areas of polar molecules at 50 °C, except for the ethyl acetate which gives a surface area on PTFE less than that on MgO or ZnO, whereas we obtained the same values for molecules adsorbed on oxides.

4. Conclusions

A new experimental method to determine the surface areas of polar molecules was proposed by coupling two classical methods, the DCA and IGC at infinite dilution. The theoretical models proposed were tested and used to obtain the best appreciation of the surface areas of such molecules.

Our results obtained from cylindrical and Kiselev models gave the best results at 50 °C in comparison with those determined by the other methods. The surface areas of adsorbed molecules obtained by using the Van der Waals model allowed us to obtain more precise results at 80 °C; whereas at higher temperature, the best result is obtained by using the Redlich–Kwong model that takes into account the thermal agitation phenomenon. We then proved an important effect of the temperature on the surface areas of molecules.

Surface areas of adsorbed molecules on solids determined by BET method and projection models are smaller than those obtained by the other models because they probably neglect the interactions between the molecules and the solid.

Finally, another new general method was proposed to calculate polar molecule areas by using the IGC technique and by assuming that the specific interactions between a polar molecule and a solid proposed by Papirer et al. and Schultz et al. are the same.

5. Nomenclature

a	Surface area of molecule
A	Constant depending of the nature of the solid substrate
AN	Acceptor number of electrons
B	Second constant depending of the nature of the solid substrate
C	Constant depending on the reference state of adsorption
DN	Donor number of electrons
D_c	Corrected flow-rate
D_m	Measured flow-rate
Isp	Specific interaction
$Isp(\text{probe})$	Specific interaction of the probe
$Isp(\text{ref.})$	Specific interaction of the reference molecule
j	Correction factor taking into account the compression of a gas
$\mathcal{N}$	Avogadro's number

P_0	Vapour pressure of a probe
P_a	Atmospheric pressure
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
γ_s	surface energy of the solid
γ_l^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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