Inverse Gas Chromatography with Film Cell Unit: An Attractive Alternative Method to Characterize Surface Properties of Thin Films

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Abstract

Inverse gas chromatography (IGC) is widely used for the characterization of surfaces. The present work describes a novel IGC tool, the recently developed film cell module, which measures monolithic thin solid film surface properties, whereas only samples in powder or fiber state or polymer-coated supports can be studied by classic IGC. The surface energy of four different solid supports was measured using both classic IGC with columns packed with samples in the powder state, and IGC with the new film cell module or the sessile drop technique, using samples in the film state. The total surface energy and its dispersive and specific components, were measured for Glass, Polyethylene, Polyamide and Polytetrafluoroethylene. Similar results were obtained for the four materials using the three different techniques. The main conclusion is that the new film cell module for IGC is an attractive alternative to the sessile drop technique as it gives very accurate and reproducible results for surface energy components, with significant savings in time and the possible control of sample humidity and temperature. This film cell module for IGC extends the application field of IGC to any thin solid film and can be used to study the effect of any surface treatment on surface energy.

Keywords: Inverse gas chromatography, film sample, surface energy, contact angle.

Introduction

Surface energy measurements are very frequently used in material sciences to investigate wettability, adhesion characteristics, specific interactions with other molecules, cohesion and coating performance [1]. The most commonly used method to achieve such measurements is the Sessile Drop Technique using a goniometer which is relatively easy to perform and inexpensive. It consists of producing a drop of liquid on a solid and measuring the angle formed between the solid/liquid interface and the liquid/vapor interface, which is called the “contact angle” (CA) [2]. This angle, measured for a minimum of three types of liquids, and the known surface energy of the liquids are the parameters that are used to calculate the surface energy of the solid sample [3]. The main disadvantage of this method is that it is unable to reflect the totality of the surface energy properties, even if multiple droplets are deposited on various locations on the sample. CA gives reproducible results, but problems of reproducibility and accuracy may occur, in case of droplets that are not axially symmetric, or with surface-accessible pores, which can decrease the droplet volume by capillary action during measurement [4,5]. To overcome these disadvantages, alternative methods of measuring surface energy must be developed. Two of the most common alternative methods are capillary intrusion of liquid analytes into the sample and analyte adsorption onto a sample bed at infinite dilution using Inverse Gas Chromatography (IGC). Capillary intrusion and conventional IGC are both restricted to the samples in the powder or fiber state and also to polymers and polymer-

coated supports, either packed in columns or deposited as a film on the inside of a column to create a capillary column. Nevertheless, a significant advance has been made recently with the development of a new system called film cell module for IGC, which is convenient for flat and monolithic samples. That is why we chose to focus on this last method as an alternative to CA measurements.

IGC is a vapor adsorption technique, which consists in an inversion of conventional gas chromatography. Physico-chemical characteristics in the stationary phase are studied by injecting specific well-characterized gaseous probes [6-8]. IGC is conventionally performed in columns containing the packed solid under investigation in the powder or fiber state. The interaction between these probes and the solid material forming the stationary phase is then investigated by determining the retention time for a given probe and used to calculate many physico-chemical properties, such as surface energies of solids [9], enthalpy and entropy adsorption [10], solubility parameter, crystallinity [11], surface heterogeneity [12], nanorugosity [11], glass transition [11] and melting temperature [7].

For surface energy determination, IGC presents many advantages compared to CA measurements: (i) the ability to quantify strong interaction occurring between the solid and the probes that cannot be characterized by contact angle measurement because of a contact angle close to zero [11], (ii) no problem of nanorugosity and surface heterogeneity [13,14], as the interactions of the probes are measured all along a wide solid surface and give mean values of interaction through the measure of the retention times, whereas CA measurements are restricted to the number of droplets deposited on the surface. Film cell module for IGC provides quite a large interacting area with gaseous probes: a relatively large rectangular sheet of flat sample (10 x 400 mm) is submitted to a gaseous flow carrying the probes, which are situated in a small groove all along the sample (iii) IGC is less time consuming, (iv) IGC is an accurate, versatile, reproducible method, with relatively easy sample preparation, (v) advanced IGC instruments have been developed with fully automated operation, humidity and temperature control, *in-situ* sample preconditioning; thus experiments may be carried out over appreciable temperature ranges, so that the temperature dependence of thermodynamic interactions can be determined.

The field of application of conventional IGC is wide. It concerns materials in the powder or fiber state and also polymers, that are either coated onto inert support and packed into columns or deposited as a uniform film on the inside of a column to create a capillary column [15]. It includes synthetic and biological polymers [8], paper and other cellulosics, fillers and pigments, flavourings and perfumes, minerals and inorganic materials [16], food products [17], packaging and coatings, pharmaceuticals and medical products [18], building materials, cosmetics and ingredients, natural and artificial fibers [19], supported catalysts and microporous material [20] and adsorbents [21]. The new film cell module for IGC is able to extend these different application fields to monolithic thin solid films.

In the present work, we compare three approaches to determine the surface energy of solids, including the dispersive

and specific components: (i) conventional IGC at infinite dilution (IGC-C) with solid samples in the powder state packed in a column as a fixed bed, (ii) two-dimension IGC with the film cell module at infinite dilution (IGC-FC) with solid samples in the film state and (iii) analysis of CA data using the Good-van Oss theory, with solid samples in the film state. The surface energetics of four different materials including polymers (Polyamide (PA), Polytetrafluoroehylene (PTFE), and Polyethylene (PE) and glass were determined. These materials all exist in both powder and film states and their surface energy was investigated by the three IGC-C methods for powders and by IGC-FC and CA for films.

To our knowledge, no study has yet been devoted to the comparison of surface energy obtained for the same material in the granular state using IGC-C columns and in the film state using IGC-FC, nor to the comparison of surface energy values obtained by IGC-FC and CA for samples in the film state.

Experimental

All materials (powders or films) were washed as below. The sample was immersed in PCC-54 (Fisher Scientifics) 2 % (v/v) for 10 minutes with an orbital agitation (100 rpm, Heidolph Rotamax 120). Then they were rinsed five times with sterile ultrapure water at 40°C for 5 minutes with the same orbital agitation. Each film sample was finally wiped with optical cleaning tissue (Whatman 105), and was dried at 40°C into an incubator. All samples were stored at room temperature.

For CA measurements, a minimum of 10 droplets were measured on each surface.

All experiments involving IGC analysis were performed in triplicate, so a standard deviation can be calculated.

Instrumentation and Reagents

CA were measured with a goniometer G40 (Krüss, Germany) at room temperature (23°C) with an accuracy of ± 2°C. The chromatographic experiments were performed using an IGC 2000 (Surface Measurement Systems, London, UK). A technical drawing of the Film-cell module for IGC-FC (Surface Measurement Systems, London, UK) is presented in Figure 1. As an external bench-top unit made from stainless steel material, the film cell module provides an interacting area of 350 x 40 mm with a 0.3 mm groove.

The apolar probes (decane (C10), nonane (C9), octane (C8), heptane (C7) and hexane (C6)) and polar probes (dichloromethane, chloroform, ethyl acetate, toluene, diiodomethane and formamide) were supplied by Sigma with HPLC purity. They were used without further purifications. Ultrapure water was obtained via a Milli Q system (Millipore, France). The relevant characteristics of both amphotheric and polar probes, including the molecular cross-sectional surface area, the acid-base character and the surface energy components are presented in Table I.

Contact angle (CA), IGC-C and IGC-FC measurements were performed on four different supports: Glass (Thermo, 1mm thick), Polyethylene (PE, Goodfellow 0.5mm thick), Polyamide-nylon 6 (PA, Goodfellow 0.5 mm thick) and Polytetrafluoroethylene (PTFE, Goodfellow 0.5 mm thick). For measuremenst by IGC-FC, the film materials was cut in 10 x 400 mm pieces, whereas IGC-C measurements in packed column were performed with the powders with particle size ranging from 100 to 150 µm of diameter. Packing is accomplished with the aid of a mechanical vibrator. For PE, PA and PTFE, both powder and film had the same chemical composition. Both powder or film glass samples were made in soda-lime-silica glass.

Methods

Determination of surface energy by CA

According to the GVOC (Good Van Oss Chaudhury) approach [3], CA were converted into surface energy components using the Young-van Oss equation (Eq.1), which ignores spreading pressure and highlights Lifshitz-van der Waals and Lewis acid/base surface free energy components.

$$\gamma_L^t\left(1+\cos\theta\right)=2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}}+\sqrt{\gamma_S^+\gamma_L^-}+\sqrt{\gamma_S^-\gamma_L^+}\right) \qquad (1)$$

Here, γ^t , γ^{LW}, γ^+ and γ^- are the total surface energy, Lifshitz-van der Waals, electron-acceptor (or Lewis-acid) and electron-donor (or Lewis-base) components of the surface free energy respectively; θ is the CA and the subscripts L and S denote the liquid and solid samples, respectively.

Equation 2 allowed accessing to the Lewis acid-base components of the surface energy:

$$\gamma^{AB}=2\sqrt{\gamma^+\gamma^-} \qquad (2)$$

Determination of surface energy by IGC

IGC was operated at “infinite dilution.

Determination of the net retention volume

The net retention volume V_N of vapor probes is then calculated using Eq.3 [22]:

$$V_N = j\times t_N \times F \text{ (ml)} \quad (3)$$

where t_N is the net retention time, calculated using Eq. (4); F ($ml.min^{-1}$) the carrier gas flow rate, at the sample temperature and j is the James and Martin compressibility factor, calculated using Eq. (5), taking into account the compression of the gas and the pressure drop upstream the column or module [23].

$$t_N = t_R - t_0 \quad (4)$$

where t_R is the experimental retention time used by a probe to cross the column or the film cell and t_0 the dead time of the column or film cell, determined through the injection of methane which does not adsorb on the solid.

$$j = \frac{3}{2} \times \frac{\left(P_i / P_0\right)^2 - 1}{\left(P_i / P_0\right)^3 - 1} \quad (5)$$

where P_i and P_0 are the inlet and outlet pressures respectively.

In practice, j is considered to be equal to 1 when using the film cell module.

Determination of the free energy of adsorption

The net retention volume V_N of vapor probes is directly related to the variation of the free energy of adsorption ΔG_{ads}, according to Eq.6

$$\Delta G_{ads} = -(R \times T \times \ln V_N) + C \quad (6)$$

where C is a constant depending on the choice of a reference state of the adsorbed probe and also on the total area of the solid accessible to the probe, R is the gas constant and T the absolute temperature. ΔG_{ads} takes into account two kinds of interactions (Eq.7): dispersive interactions ΔG_{ads}^{D}, corresponding to London forces and specific interactions ΔG_{ads}^{SP}, which consists mostly out in Lewis acid-base contributions.

$$\Delta G_{ads} = \Delta G_{ads}^{D} + \Delta G_{ads}^{SP} \quad (7)$$

To obtain the dispersive as well as the specific parts of ΔG_{ads}, different apolar and polar vapor molecules respectively are injected and their net retention volume V_N determined.

Determination of the dispersive component of the surface energy

In case of apolar probes, like *n*-alkanes, which can only interact by dispersive interactions, V_N is related to ΔG_{ads}^{D} by Eq.8, which uses the relation of Fowkes [24]:

$$\Delta G_{ads}^{D} = -R \times T \times \ln V_N + C = -2N_A (\gamma_S^D)^{\frac{1}{2}} \times a \times \left(\gamma_L^D\right)^{\frac{1}{2}} + C' \quad (8)$$

where N_A is the Avogadro constant, R the gas constant, a the molecular cross-sectional area of probes adsorbing on the solid surfaces (m^2) and γ_L^D the dispersive component of the liquid probe surface energy and γ_S^D the dispersive

component of the surface energy of the solid. If a series of alkanes is injected, γ_S^D can be derived from the slope of the fitted line, which is called the "alkane line" in a plot of $RTlnV_N$ versus $a\left(\gamma_L^D\right)^{\frac{1}{2}}$.

Determination of the specific component of the surface energy

The experimental points for the polar probe molecules are located above the alkane line in the surface energy plot. The vertical distance between each point and the alkane straight line represents the specific contribution of the interaction, which is expressed as the specific free energy ΔG_{ads}^{SP}.

On the whole, this approach for acid-base calculations used in IGC is the van Oss concept, which provides acid and base numbers in the same units as the dispersive surface energy, according to Eq.9:

$$\Delta G_{ads}^{SP} = 2 \times N_a \times a \times \left(\left(\gamma_L^+ \times \gamma_S^-\right)^{\frac{1}{2}} + \left(\gamma_L^- \times \gamma_S^+\right)^{\frac{1}{2}} \right) \quad (9)$$

where ΔG_{ads}^{SP} is the specific component of the surface energy (mJ/mol), N_A is the Avogadro constant, a the molecular cross-sectional area of adsorbates (m^2), γ_L^+ and γ_L^- (mJ/m²) the electron acceptor (acid) and electron donor (base) parameters of the probe molecule, γ_S^+ and γ_S^- (mJ/m²) the electron acceptor (acid) and electron donor (base) parameters of the surface. Then γ_S^+ and γ_S^- can be calculated thanks to two couples of complementary polar probes: dichloromethane (DCM)/ethyl acetate (EA) and toluene (T)/chloroform (CF), where γ_S^- is equal to zero for DCM and CF and γ_S^+ is equal to zero for EA and T.

The specific or polar component of surface energy γ_S^{SP} (mJ/m²) can then be calculated from the γ_S^+ and γ_S^- according to the Eq. 10. Finally, the total surface energy γ_S^t is also accessible through the Eq. 11.

$$\gamma_S^{SP} = 2 \times \sqrt{\gamma_S^- \times \gamma_S^+} \quad (10)$$

$$\gamma_S^t = \gamma_S^{SP} + \gamma_S^D \quad (11)$$

A conditioning period of 12 hours was applied for each experiment to equilibrate the chromatographic column or the module with their sample *in situ* at constant conditions of temperature (40°C) and gas flow (helium, 10 mL/min) with a relative humidity (RH) of zero, except when the effect of RH on surface energy was studied. In this case RH was equal

to values ranging from 10 to 50% in the carrier gas. The optimal quantity of probes to obtain an infinite dilution mode and sharp and symmetrical peaks were obtained at $p/p_0 = 0.025$, with p being the partial pressure of the solute in the gas phase and p_0 the saturation vapor pressure of the solute.

Results

Comparison of the surface energy obtained for materials in either the granular state using IGC-C columns or in the film state using IGC-FC

The main aim of this paper is to investigate the use of a new system called film cell module for IGC, to study the surface energetics of flat and monolithic samples. In order to assess whether meaningful data were obtained using this new module, the surface energetics of the same materials in either the granular state or in the film state were assessed by using respectively IGC-C and IGC-FC.

The IGC-FC method allows direct access to the surface energy of solid films. However, the use of the film cell module, which is made of stainless steel (Figure 1), leads to a measurement bias because it is not inert. The empty module has a significant polar component for its surface energy that must be substracted by performing a blank. The dispersive component is, however, negligible. In contrast, IGC-C columns are made of inert glass and a blank is not necessary.

The results from both IGC-FC and IGC-C are summarized in Table II; the values of the total surface energy calculated from the IGC-FC experiments are in good agreement with those calculated from IGC-C for the different tested supports, except for PA. For this material, these values are equal to 43.8±1.8 mJ/m^2 from IGC-C and 48.5±2.3 mJ/m^2 from IGC-FC, respectively. The magnitude of all values determined here for all materials compared reasonably well with previously reported values in the literature [25].

For all the surface energy components measured in IGC-FC the calculated values are not significantly different from those obtained in IGC-C (Table II), except for PA and for the electron-donor component of glass. For PA, both dispersive and specific components of surface energy obtained from IGC-FC were higher than the ones obtained from IGC-C. For glass, the electron-donor component from IGC-C was higher than from IGC-FC.

Comparison of the surface energy obtained by IGC-FC and CA for materials in the film state

CA is one of the most commonly used techniques in the characterization of surface energetics and wettability of materials in the film state. It was therefore used as a point of comparison with IGC-FC.As observed in Table II, the values of the total surface energy calculated from the CA experiments corroborate the surface energy trends established with IGC-FC and give somewhat lower absolute values for these numbers, in case of the three substrata with the lowest

surface energy: PTFE, PE and PA. A GVOC approach was used for CA experiments, which allows the conversionof CA into γ_S^{LW} (Lifshitz-van der Waals), and γ_S^+ and γ_S^- (Lewis acid and base) surface energy components. It is recognized that the Lifshitz-van der Waals contribution is primarily due to dispersion forces or London interactions, although small contributions resulting from the presence of permanent dipoles may also be accounted for in this term (induction or Debye and orientation or Keesom interactions) [26]. Therefore, it is relevant to compare values obtained from CA and values obtained from IGC-FC.

For PTFE, PE and PA, the γ_S^D obtained using IGC-FC were slightly superior to the γ_S^{LW} values obtained from CA: Interestingly, in the case of glass, a higher value for the total surface energy (γ_S^t = 56.2 ± 0.3 mJ/m²) was calculated with CA measurements, compared to IGC-FC, for which a value of 47.9 ± 3.3 mJ/m² was obtained (Table II). This difference is statistically significant with a *p-value* of 0.00021 (calculated from Student test). It arose only from the γ_S^- values that are equal to 11.0 ± 2.6 mJ/m² with IGC-FC and 54.1 ± 2.6 mJ/m² with CA, whereas γ_S^D and γ_S^{LW} values on the one side and γ_S^+ values on the other side were very similar.

Effect of relative humidity on the surface energy of glass measured by IGC-FC

The influence of the relative humidity (RH) on the evolution of the specific component of the surface energy for glass was examined using IGC-FC.

The results for the total surface energy and its different components measured by IGC-FC as a function of RH are presented in Figure 2. On the right of Figure 2 are also presented the results for the total surface energy and its different components for glass measured by CA with atmospheric RH equal to 50%. For glass from IGC-FC measurements, it appears that the electron-donor component significantly increases with the RH. On the other hand, the dispersive and electron-acceptor components maintain similar values all along the humidity gradient. The values calculated for the electron-donor component increased from 11.0 mJ/m² to 66.79 mJ/m² in accord with the gradient of RH in the gaseous stream and from 0 to 50 %RH in IGC-FC, and showed a linear tendency between 10 and 50 %RH, with a slope equal to 15.3 (mJ/m^2)/(%RH). The increase in the electron-donor component with RH may be due to the interaction of the probes with water molecules adsorbed on the surface and the formation of silanol (Si-O-H) sites by chemisorption. For glass from CA measurements taken at room temperature with atmospheric RH equal to 50%, it appears that the value of the electron-donor component is close to the one obtained with IGC-FC at 30 and 40%RH.

Discussion

As mentioned in the results part, the values obtained for surface energetics by IGC-FC corroborate those surface energy trends established with IGC-C and the magnitude of these numbers compare reasonably well. Some significant differences between the two methods exist however for the absolute values of both dispersive and specific components of surface energy found for PA and also for the electron-donor component of glass. These differences may arise from an effect of the geometry of the materials on the interpreted surface energetics, as shown previously for different works using IGC. For example, Guillet et al. reported differences for polystyrene between studies using pure polymer packed in a column and or capillary columns coated on the inside with polymer [15]. They found that specific retention volume values were slightly higher for an open column than for a packed column, possibly because of the higher specific surface area available in the open column. Jones et al. mention that milling increased the dispersive surface energy and surface acidity of lactose and several respiratory drugs. These effects could be ascribed to the introduction of surface structural defects or to the disruption of particle flaws exposing surfaces rich in hydroxyl groups in the case of lactose [18].

The differences between results from CA and IGC are well known and the discussion about this point is out of the scope of this paper. These differences arise from the vastly different energetics between the two systems, involving gas/condensed phase interaction for IGC and condensed phase/condensed phase interaction for CA. In the present study, another difference was introduced between the two systems through the difference in RH values during experiments:

RH was not controlled during CA experiments and was equal to the ambient atmospheric RH which was 50% that day. This is one of the reasons explaining the important difference in the γ_S^- values found for glass using CA or IGC at RH equal to 0. Glass is by far the most hydrophilic material among the four studied. It is composed mainly of silica, and previous studies have shown that water can rupture siloxane (Si-O-Si) bonds via dissociative chemisorption, forming silanol (Si-O-H) sites, in particular at the first stage of humidification [27,28]. This chemical change occurring at the surface of glass also affects the specific component of the surface energy. For this reason, the effect of RH on the surface energy was studied for glass by IGC-FC. It appears that when increasing the RH from 0 to 50% in IGC, the difference in the γ_S^- values found for glass using CA or IGC-FC decreases. However, considering that temperature is changed from 23°C to 40°C between CA and IGC-FC experiments, the quantity of adsorbed water on glass for a same RH is higher in case of IGC-FC, undercutting the relevance of the exact comparison of results from CA and IGC-FC at the same RH.

Conclusion

The new film cell module for inverse Gas Chromatography experiments, presented in this work, enables to obtain meaningful data for the surface energetics of flat and monolithic samples, for solid materials with varying surface properties: PTFE, PE, PA and glass. In comparison with CA measurements, it offers the possibility to control the temperature and the RH perfectly during automated and rapid experiments, including *in situ* conditioning.

Thanks to these preliminary results, it can be concluded that IGC-FC appears as a viable method. However, more extensive study is needed to identify the origin of differences with standard IGC-C, since the differences in surface geometry may also have an influence on the interpreted surface energetics. IGC-FC extends the possibility of IGC to flat and monolithic samples. The analysis can be performed directly on two dimensions samples, without any prior preparation. The field of application of IGC-FC is large and includes the easy analysis of the influence of cleaning or painting on the surface energy parameters of solid surfaces, important in a wide variety of industries.

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358 Figure 1: Technical drawing of the film cell module for iGC (35x400x11 mm). The arrows show gas flow.

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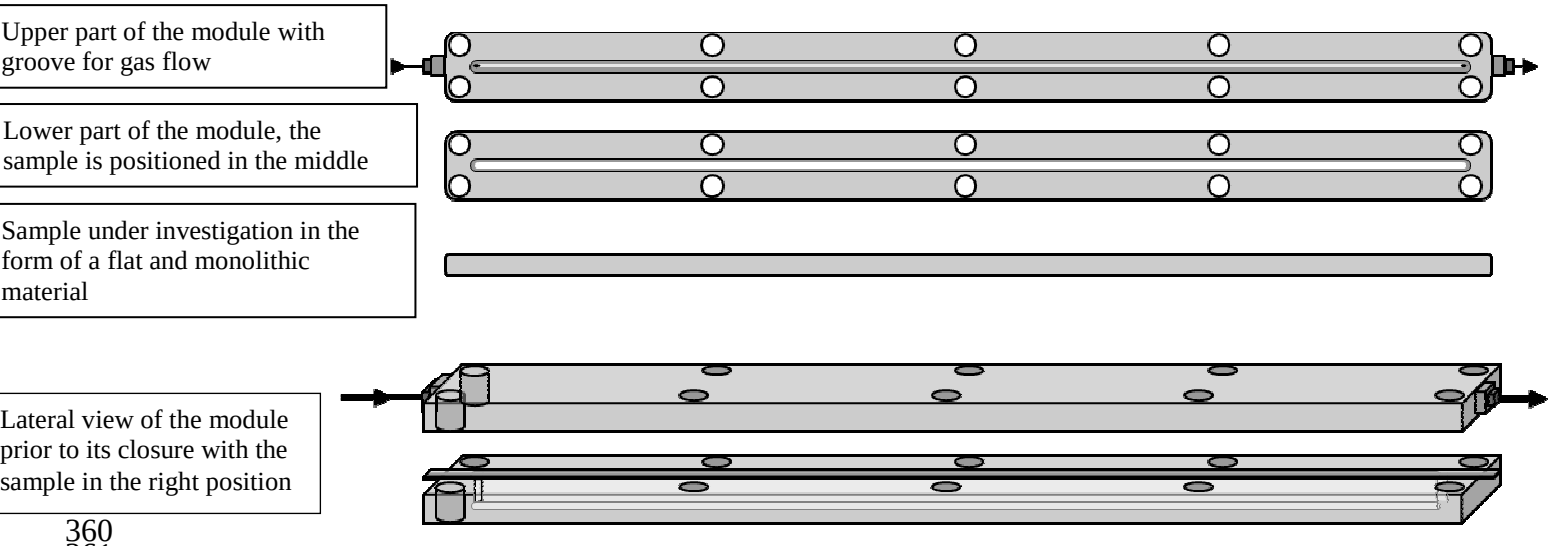

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363 Figure 2: Surface energy components measured on Glass, depending on a RH gradient established into the film cell
364 module during iGC experiments and values obtained with CA measurements at “ambient” RH.

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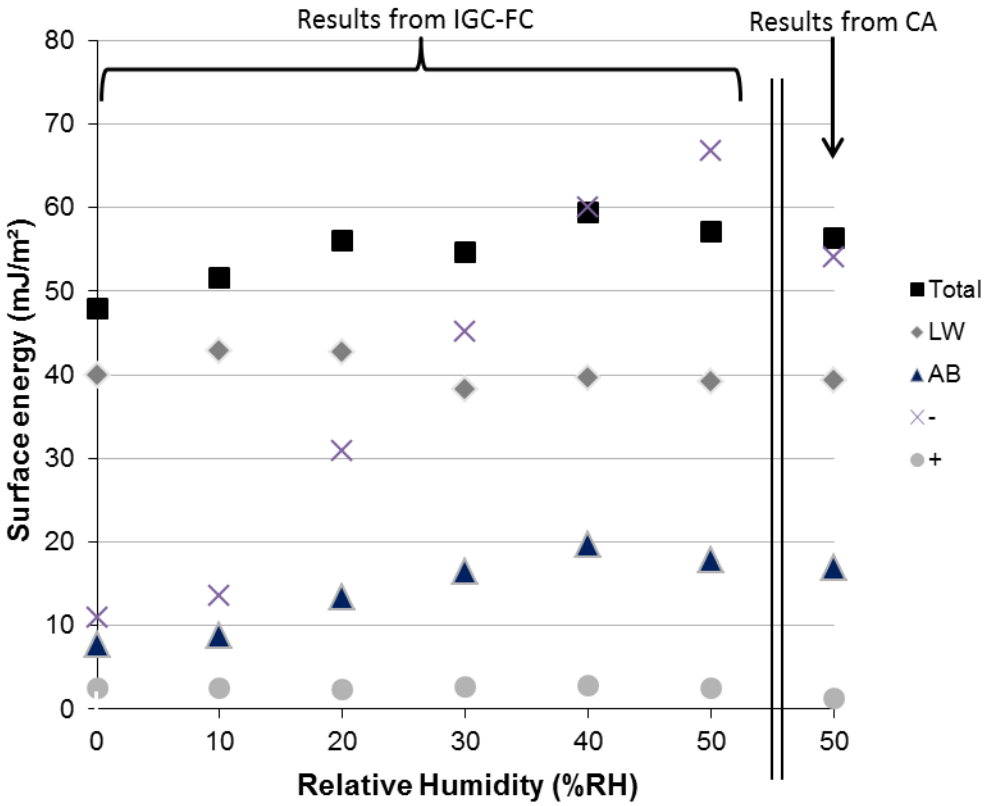

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Table I: Acid-base character and values of cross sectional area and surface energy components of amphoteric and polar probes used in contact angle and IGC experiments. Values from [29-33], DCM = dichloromethane, EA = ethyl acetate, T = toluene, CF = chloroform.

Solvents - probes	**Molecular cross-sectional surface area "a" (m^2)**	**Surface energy (mJ/m^2) of the liquid probes**			
		total surface energy γ_L^t	dispersive component γ_L^D	electron acceptor parameter γ_L^+	electron donor parameter γ_L^-
***n*-alkanes**					
C6	5.15×10^{-19}	18.4	18.4	0.0	0.0
C7	5.73×10^{-19}	20.3	20.3	0.0	0.0
C8	6.30×10^{-19}	21.3	21.3	0.0	0.0
C9	6.92×10^{-19}	22.7	22.7	0.0	0.0
C10	7.44×10^{-19}	23.9	23.9	0.0	0.0
Contact angle					
water	/	72.8	21.8	25.5	25.5
formamide	/	58.0	35.6	2.3	39.6
diiodomethane	/	50.8	50.8	0.0	0.0
iGC					
DCM	2.99×10^{-19}	26.5	26.5	5.2	0.0
EA	3.29×10^{-19}	23.9	23.9	0.0	19.2
T	4.20×10^{-19}	28.5	28.5	0.0	2.3
CF	3.51×10^{-19}	27.2	27.2	3.8	0.0

Table II: Calculated values of surface energy for five materials, PA = polyamide-6, PE = polyethylene, PTFE = polytetrafluoroethylene and Glass. [a] Materials at powder state. [b] Materials at film state. Standard deviations were calculated with n ≥ 10 measurements.

Materials	γ_S^t **(mJ/m^2)**	γ_S^{LW} **(mJ/m^2) (CA)** γ_S^D **(mJ/m^2) (iGC)**	γ_S^{SP} **(mJ/m^2)**	γ_S^+ **(mJ/m^2)**	γ_S^- **(mJ/m^2)**
iGC columns[a] (iGC-C)					
PTFE	19.5 ± 2.3	19.1 ± 2.3	0.4 ± 0.0	0.1 ± 0.0	0.5 ± 0.1
PE	32.2 ± 2.1	31.6 ± 2.1	0.6 ± 0.0	0.1 ± 0.0	0.9 ± 0.2
PA	43.8 ± 1.8	41.9 ± 1.7	1.9 ± 0.2	0.2 ± 0.1	4.1 ± 2.5
Glass	46.7 ± 1.6	39.8 ± 1.8	7.0 ± 0.3	0.5 ± 0.2	22.8 ± 1.8
iGC film-cell[b] (iGC-FC)					
PTFE	21.1 ± 3.1	21.0 ± 3.2	0.1 ± 0.1	0.0 ± 0.0	0.5± 0.3
PE	32.9 ± 1.5	31.0 ± 1.5	1.9 ± 0.6	0.3 ± 0.3	2.7 ± 1.2
PA	48.5 ± 2.3	44.7 ± 2.6	3.8 ± 1.2	0.4 ± 0.3	8.9 ± 1.7
Glass	47.9 ± 3.3	40.0 ± 2.2	7.8 ± 1.1	2.5 ± 2.1	11.0 ± 2.6
Contact angle[b] (CA)					
PTFE	17.1 ± 0.9	15.9 ± 0.6	1.2 ± 0.3	0.2 ± 0.1	1.9 ± 0.5
PE	32.5 ± 2.7	29.3 ± 1.5	3.2 ± 1.2	0.8 ± 0.3	3.4 ± 1.6
PA	42.4 ± 0.9	40.4 ± 0.8	2.0 ± 0.2	0.1 ± 0.0	11.5 ± 1.5
Glass	56.2 ± 0.3	39.4 ± 1.6	16.8 ± 1.9	1.3 ± 0.3	54.1 ± 0.2