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Coupling of inverse gas chromatography at infinite dilution (IGC-ID) with a controlled modification of a solid surface

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Abstract

This paper presents a new method for studying the surface of a heterogeneous solid by inverse gas chromatography at infinite dilution (IGC-ID). After saturating the high-energy sites by impregnation with a suitable polymer, the chromatographic probes visit the low energy sites, which are not visible by conventional IGC-ID. This method has been used to study the two types of surface of talc: lateral and basal surfaces. In the second part of the paper the influence of the structure of the polymer on the impregnation is examined. In particular it is shown that a polymer with a linear structure is more able to fit a rough surface than is a branched or a cyclic polymer.

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1. Introduction

Inverse gas chromatography at infinite dilution (IGC-ID) is a useful method for exploring the thermodynamic surface properties of a homogeneous solid at the molecular scale. The complexity of the interactions between probes and the surface of a solid depends on the amount of probe injected. Further theoretical details can be found elsewhere [1]. In IGC-ID, very small amounts of probes are injected in such a way that the interactions between probe molecules can be considered to be negligible and only the interactions between the surface of the solid and an isolated probe molecule are important. However, a limitation of IGC-ID appears in the case of a heterogeneous surface where IGC-ID only gives

access to apparent thermodynamic data because probes mainly interact with the high-energy adsorption sites [2]. We try to take advantage of this limitation by coupling IGC-ID with a progressive absorption impregnation of a suitable polymer of the sites having the highest energy. A polymer is used to progressively saturate the more interactive sites by preferential adsorption, thus causing the probes to access the less energetic sites remaining free. So, by progressively increasing the amount of polymer added to the solid, the probes will access different energy sites on the surface of the solid. We have applied this method to talc which is a phyllosilicate with a heterogeneous lamellar structure, having two kinds of surface:

- weak energetic basal surfaces with basic Si–O–Si groups, and
- more energetic lateral surfaces with acidic Si–OH groups and residual magnesium cations.

The intention is to use a basic polymer to interact

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preferentially with the lateral acidic surfaces of the talc. When sufficient polymer is adsorbed on the surface to saturate the lateral surfaces, the probes will then access the less energetic sites on the basal surfaces. Therefore the surface energy of the basal surfaces, inaccessible to the probe with conventional IGC-ID, are then determined.

Impregnation of the surface of a solid with a polymer also allows the characterisation of solid–polymer interactions. Here we study effects induced by three types of basic polymers: linear, branched and cyclic which have different degrees of surface steric hindrance, i.e. polyethyleneglycol 20 000 (PEG), polyethylvinylether 3800 (PEVE), and polystyrene 230 000 (PS).

2. Experimental

The talc used in the experiments was provided by the Luzenac Europe Company and had an average particle size of 10 μm , as measured by a Micromeritics Sedigraph 5100. The PEG was supplied by Fluka and the two other polymers, PEVE and PS, by Aldrich. High purity dichloromethane obtained from Fisher Scientific International Company was used for the preparation of the polymer solutions. Stainless steel chromatographic columns with an inside diameter of 5.3 mm and a length of 10 cm, closed at the output end with a stainless steel frit of 0.5 μm porosity, filled with ~ 2 g of talc were used in the tests.

Two Hewlett-Packard 6890 gas chromatographs were used, each fitted with two flame ionisation detectors (FID). The carrier gas was helium with a flow of ~ 30 ml/min. The injector and detector were heated to 150 $^{\circ}\text{C}$. All the columns were conditioned at 120 $^{\circ}\text{C}$ overnight and the analyses made at 100 $^{\circ}\text{C}$. Net retention times were calculated by subtracting the retention time of a non-retained molecule, methane, from the retention time of the probe. The probes used were linear alkanes ($\text{C}_n\text{H}_{2n+2}$ with $5 \leq n \leq 12$) and cyclooctane a branched alkane; all the probes are therefore apolar.

The samples were prepared by controlled impregnation of talc with the different polymers (PEG, PEVE, PS) using the following method. The mass of talc required to fill the column (~ 2 g), was put in a

beaker and mixed with a given volume of the polymer solution until the mixture became homogeneous (~ 5 min). The polymer solutions cover ranges, respectively, from 0.01 to 30, 0.01 to 80, and 0.07 to 32 mg for the PEG, PS and PEVE per gram of talc. After evaporation of the solvent in a vacuum oven, the column was filled with the polymer impregnated talc. These columns were maintained under a nitrogen atmosphere to prevent polymer oxidation.

3. Results

In the first part of the study, the evolution of both the dispersive component of the surface energy, γ_s^d , and the nanomorphological index, I_m [3], were studied as a function of the amount of PEG added to the talc (Fig. 1). The γ_s^d is a measurement of the dispersive London forces between the surface of the solid and linear alkanes injected as probes. The I_m reflects size exclusion effects, or a measurement of the surface of the solid that can be reached by a branched alkane. It is determined by the injection of a branched or cyclic probes. In the present work, the I_m was determined using cyclooctane as injected probe.

The impregnation ratio has no real meaning from a molecular point of view, and the coverage ratios of the monomer unit expressed in MU/nm^2 are calculated using the following formula:

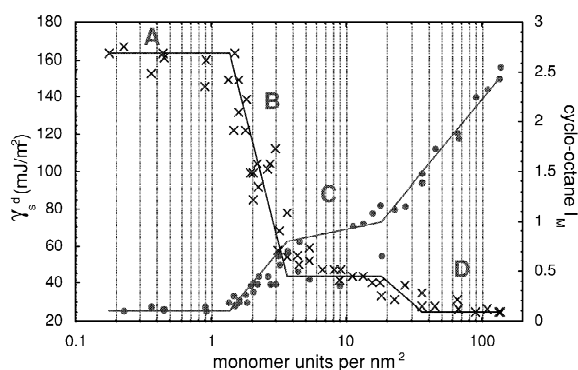


Fig. 1. Evolution of the dispersive component of the surface energy (γ_s^d) (\times) and the nanomorphological index I_m (\bullet) for a reference talc impregnated with different ratios of PEG.

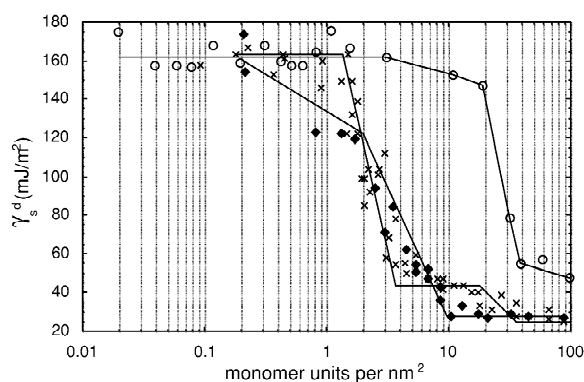


Fig. 2. Evolution of the dispersive component of the surface energy (γ_s^d) for a reference talc impregnated with different ratios of PEG (\times), PEVE (\blacklozenge) or PS (\circ).

$$n_{\text{MU}} + \frac{6023\tau}{M_{\text{MU}}S}$$

where τ (%) is impregnation ratio expressed as a percentage; n_{MU} is polymer monomer unit number per nm^2 of talc; M_{MU} is molecular mass of the monomer unit: 44 g per MU for the PEG, 104 g per MU for the PS, 72 g per MU for the PEVE; S is specific area of powder in m^2/g . For the talc, a value of $3 \text{ m}^2/\text{g}$ was retained as determined by BET measurements performed by argon adsorption.

The second part of this paper examines the influence of the steric hindrance of different polymers on the evolution of the thermodynamic surface properties of the impregnated talc. In particular the effect of PEG, which has a linear structure, is compared to the effects shown by two other basic polymers: a branched polymer (PEVE) and a cyclic polymer (PS) (Fig. 2).

4. Discussion

4.1. Impregnation of the surface of a reference talc with PEG

The impregnation of the surface of a reference talc with an increasing amount of PEG allows following the evolution of γ_s^d and I_m . The results, which have

also been fully commented on in a previous paper [4], present four domains (Fig. 1).

In domain A, with no polymer or at very low polymer impregnation ratios, both γ_s^d and I_m remain constant. The high value of γ_s^d ($160\text{--}170 \text{ mJ}/\text{m}^2$) is attributed to the insertion of the linear alkanes into the slot-like sites situated on the lateral surfaces. The low I_m corresponds to size exclusion effects. The linear alkane is able to insert partially into porous sites whereas a substituted probe such as cyclooctane is excluded. When the PEG ratio is increased, this basic polymer interacts preferentially with the acidic hydroxyl groups on the lateral surface. As long as the amount of PEG is not enough to cover all the high energy sites on lateral surfaces, γ_s^d and I_m remain constant. At the end of region A, it may be considered that all the lateral surfaces have been covered.

In domain B, γ_s^d decreases and I_m increases with increasing PEG impregnation ratios. These changes in γ_s^d and I_m can be attributed to the filling of the wedge-like sites and the structural defects situated between the talc crystallites. The size exclusion effect disappears (increase of I_m) with the increase in the amount of polymer and the filling of these sites.

In domain C, γ_s^d is constant and equal to $45 \text{ mJ}/\text{m}^2$. This value, already obtained by contact angle measurements [5], is the energy of the basal surfaces. At the end of the region C, I_m is equal to 1 and the amount of polymer deposited on the surface of the solid corresponds to a mono-layer of monomer units. It may be assumed that the whole surface of the solid is covered with a mono-layer of PEG monomer units.

In domain D, multi-layers of PEG monomer units are formed. γ_s^d becomes equal to $25 \text{ mJ}/\text{m}^2$ (value already obtained on silica impregnated with a high ratio of PEG) which corresponds to the interactions of the probes with a thick layer of PEG. I_m increases and exceeds the value of 1, which reflects the absorption of the probe in a thick film of polymer.

The impregnation by PEG of the surface of the talc seems to be sensitive not only to the surface morphology, but also to the chemical functions. PEG is able to insert partially into the slot like sites in the lateral surfaces or in the structure defects, such as grain joints between the talc crystallites. In addition, this basic polymer interacts preferentially with the

acidic sites on the lateral surfaces, causing the probes to access the less energetic free sites on basal surfaces of the talc, inaccessible by conventional IGC-ID.

The influence of the chemical structure of the polymer on the evolution of γ_s^d and I_m with the impregnation of talc may be compared with the influence of two other basic polymers: a branched polymer (PEVE) and a cyclic polymer (PS).

4.2. Impregnation of the surface of a reference talc with PEVE and PS

The plateau value of γ_s^d at 160 mJ/m², determined with low impregnation ratios of PEG, is not observed with PEVE. This is also the case for the plateau at 45 mJ/m², attributed to the coverage of the basal surfaces, which does not occur with PEVE. Despite the fact that the PEVE is a basic polymer like PEG, these two polymers differ notably by their stereochemistry. PEG has a linear structure and PEVE has some branches from the linear chain and asymmetric carbons. Because of its structure and its steric hindrance, PEVE can not fit a rough surface as easily as can linear PEG.

The curve of γ_s^d as a function of the impregnation ratio of PS presents a completely different shape from the two others. This polymer is unable to hide the high-energy sites until a high degree of adsorption coverage is achieved. The high value of γ_s^d remains constant until 20 MU of PS. The stereochemistry of the macromolecular chain and the low potential interaction with the lateral surfaces can explain the behaviour of the PS. It is probable that the polymer first covers the basal surfaces, which are

not visible in IGC-ID, rather than the lateral surfaces which alone contribute to the high value of γ_s^d . After 20 MU, the amount of PS is so great that it almost covers all the surface of micro-crystallites and γ_s^d decreases to reach the energy of a talc surface entirely covered by PS.

The differences observed between the polymers are attributed to their steric hindrance even though the molecular masses of the three polymers used are very different. In a previous study [6], polymer impregnations were made with PEG with a range of molecular masses (2000, 20 000, 35 000, 100 000). The molecular mass of the polymer was found to have no influence on the evolution of the surface properties of talc as a function of the impregnation ratio. In addition, a pyrogenic silica was impregnated with PEG, PEVE and PS and the γ_s^d curves were found to present the same form with one break point on each curve. It may be concluded that the molecular masses of these different polymers do not influence the results.

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