

Surface properties of low specific surface powders using inverse gas chromatography

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Abstract

Inverse Gas Chromatography (IGC) is used to study the influence of relative humidity and chemical treatment with sulfochromic acid on the surface properties of glass beads. The humidity of the carrier gas to the chromatograph is controlled by means of a specially designed humidity generator to allow investigation of the surface of powders attributed to the progressive coverage by water molecules. The solid under test is glass beads with a very low specific surface and the properties studied are the specific surface, thermodynamic parameters and the proportions of silanol and siloxane groups on the surface.

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1. Introduction

Many studies have been made of the influence of water adsorption on the surface properties of solids, for example pharmaceutical excipients such as sugars [1,2], food products like wheat and soy flour [3,4], cotton [5], or mineral solids [6]. This list is far from exhaustive.

Two indirect techniques are usually used for the surface energy of solids: vapour adsorption measurements using probe vapours, and wetting measurements using liquid probes [7]. The measurement of contact angles suffers from very poor reproducibility, whereas vapour adsorption techniques give good results.

Amongst the vapour adsorption techniques Inverse Gas Chromatography (IGC) is getting increasing attention as it offers several advantages such as the possibility of using a variety of probes and a large range of temperatures. The term “inverse gas chromatography” was introduced to denote that the interest is in the stationary phase in the column which may be a powder, a filler, a polymer material.

Contrary to conventional Gas Chromatography (GC) where the stationary phase serves to separate and identify the various gaseous components, IGC uses specific solute probes to determine interactions between the solutes and the solid column packing material under investigation [8]. There are two ways to perform IGC: infinite dilution (ID) [9] or finite solute concentration (CF) [10]. In the first mode, a very small amount of probe vapour, at the limit of detection of the flame ionisation detector (FID) is injected in the column and its retention volume determined. Under these conditions, Henry's law can be applied and the proportion of adsorbed probe, and therefore the retention volume, is independent of the probe concentration. In this case the injected probe molecules will explore the entire surface of the column packing and retention times will mainly reflect interactions with the strongly active sites on the solid surface examined. In finite solute concentration (CF) a liquid probe is injected instead of vapour which leads to the formation of monolayer of probe on the solid surface. In this case the finite solute concentration allows the determination of desorption isotherms and is a suitable method for evaluating the heterogeneity of the surface energy of powders.

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Previous studies [11–14] have been made on silicas and glasses in infinite dilution mode to study the influence of chemical grafting on the surface properties. The conclusions of this work underline the importance of the silanol groups on the solid surface. Here, we propose to study the influence of the relative humidity p/p^0 by IGC-ID on glass beads. The interest of these solids is their very low specific areas, less than $0.5 \text{ m}^2/\text{g}$, the objective being to test the limits of the IGC depending on the particle size. We determine the free energies, enthalpies and entropies of adsorption of apolar probes under different levels of humidity. Acid-base probes were also used to measure the acid-base characteristics of the solid surface. Secondly, we analyse the effect of a sulfochromic acid treatment on the surface properties of these glass beads.

2. Theory

Even though many publications have presented the theory of inverse gas chromatography at infinite dilution, it seems useful, to clarify the discussion and the interpretation of the results, to give a short description of the technique.

2.1. Principles

Inverse gas chromatography consists in measuring the chromatographic retention times of probes of known properties passing through a chromatography column packed with the solid material under test. The retention time of these probes, a function of the retention volumes, is related to the affinity of the probes for the solid surface. The retention volume V_N is readily calculated from the retention time by the following equation:

$$V_N = (t_R - t_O) \times D_c \quad (1)$$

where: D is the corrected flow rate of the carrier gas, t_R and t_O are the retention times of the probe and methane, respectively.

The specific retention volume is usually used to compare results of different columns and temperatures. This volume corresponds to the retention volume normalised to a temperature of 273 K and to 1 g of powder.

$$V_g = \frac{273.5 \times V_N}{T \times m} \quad (2)$$

where m is the amount of powder in the column and T the measurement temperature.

The specific retention volume is related to the variation of the free energy of adsorption ΔG_{ads} in the following way:

$$\Delta G_{\text{ads}} = - (R \times T \times \ln V_g) + C \quad (3)$$

Here C is a constant that depends on the choice of a reference state of the adsorbed probe and also on the total

area of the solid accessible to the probe. Analyses made at different temperatures and the variation of ΔG_{ads} with the temperature, allow the determination of the enthalpy of adsorption:

$$\Delta H_{\text{ads}} = -R \frac{\partial \ln V_g}{\partial \left(\frac{1}{T}\right)} \quad (4)$$

The entropy of adsorption may be related to the enthalpy and the free energy of adsorption by the following equation:

$$\Delta S_{\text{ads}} = \frac{(\Delta H_{\text{ads}} - \Delta G_{\text{ads}})}{T} \quad (5)$$

2.2. The dispersive component of the surface energy

Generally, the ΔG_{ads} takes into account two kinds of interactions: dispersive interactions (London forces) and acid base interactions (hydrogen bonding among others):

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\text{d}} + \Delta G_{\text{ads}}^{\text{sp}} \quad (6)$$

The injection of alkanes allows determination of the dispersive component $\Delta G_{\text{ads}}^{\text{d}}$ since these molecules can only interact by dispersive interactions. As the ΔG_{ads} varies linearly with the number of carbon of the n -alkane, it is possible to determine the incremental value $\Delta G_{\text{ads}}^{\text{CH}_2}$ which does not depend on the arbitrary choice of the standard reference state of the adsorbed alkane:

$$\Delta G_{\text{ads}}^{\text{CH}_2} = -RT \ln \left(\frac{V_{n+1}}{V_n} \right) \quad (7)$$

Here V_n and V_{n+1} are the net retention volumes, respectively, of the alkanes with n and $n+1$ atoms of carbon.

The free energy of adsorption can be related to the work of adhesion W_a between the probe and the solid surface:

$$\Delta G_{\text{ads}} = -NaW_a \quad (8)$$

where N is Avogadro's number and a the surface area of an adsorbed probe molecule.

When alkane probes are used, the dispersive interactions are dominant in the work of adhesion which can be related to γ_s^{d} and γ_1^{d} , the dispersive components of the solid and of the injected probe, respectively [15]:

$$W_a = -\frac{\Delta G_{\text{ads}}^{\text{CH}_2}}{Na} = 2\sqrt{\gamma_s^{\text{d}}\gamma_1^{\text{d}}} \quad (9)$$

According to Doris and Gray, and by combining Eqs. (7) and (10), the dispersive component of the surface free energy can be calculated as follow:

$$\gamma_s^{\text{d}} = \frac{(\Delta G_{\text{ads}}^{\text{CH}_2})^2}{4N^2 a^2 \gamma_{\text{CH}_2}} \quad (10)$$

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