



ELSEVIER

Journal of Chromatography A, 969 (2002) 323–327

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination of surface heterogeneity profiles on graphite by finite concentration inverse gas chromatography

Frank Thielmann*, Duncan Pearce

Surface Measurement Systems Ltd., 3 Warple Mews, Warple Way, W3 0RF London, UK

Abstract

Inverse gas chromatography (IGC) is an established tool in the determination of the adsorption potential distribution function. This function reflects the energetic heterogeneity profile of a surface and therefore provides interesting information on the nature and population of different surface sites. IGC is shown to be a fast and accurate technique for the determination of the adsorption potential distribution function of two different graphite samples. In this paper the adsorption of acidic and basic organic vapours is studied. Unlike heterogeneity profiles determined by nitrogen measurements, experiments with polar vapours can provide additional information on the adsorption mechanism and polar sorption sites. The heterogeneity profiles of all probes used are significantly different from one another and allow discreet energy levels to be distinguished. Chemically different probes reveal different adsorption mechanisms for the graphite surface.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Surface characteristics; Adsorption; Energy heterogeneity; Graphite; Inverse gas chromatography

1. Introduction

There exist two types of surface heterogeneity: structural and energetic. A typical example of a structural heterogeneity is a wide pore size distribution. It is mainly a geometrical effect determined by the relation between the probe molecule size in comparison to the pore diameter. Energetic heterogeneity occurs with a wide distribution of various surface sites of different energetic levels. Such a heterogeneity profile can be represented by an energy distribution function [1].

The energy distribution function is an important

parameter in the characterisation of solids since it can provide important information on surface property variation. A heterogeneity profile constitutes an energy “map” of the material surface. Such information allows a prediction of product properties, especially in the formulation of blends, composites or coatings. From this point of view heterogeneity profiles could potentially be applied to the identification of certain components, for instance in blends. However, this requires a better understanding of the adsorption of probe molecules of different nature (dispersive, acidic, basic). Accordingly, in this study the adsorption potential distribution function of two different graphite materials is determined for polar and non-polar probe molecules. Graphite is a particularly interesting example since it is known to have, energetically, a fairly inhomogeneous surface despite the absence of significant porosity effects.

*Corresponding author. Tel.: +44-20-8749-4900; fax: +44-20-8749-6749.

E-mail address: frank@smsuk.co.uk (F. Thielmann).

2. Theory

Generally, an energy distribution can be determined either from the pressure or temperature dependence of adsorption. The temperature method has been shown to be successful in the characterisation of heterogeneity profiles of highly energetic surfaces. Typical examples involve strong acid–base interactions between surfaces and probe molecules [2] or high adsorption potentials due to microporosity [3].

The pressure dependence method, however, is more appropriate for the determination of heterogeneity profiles of less energetic surfaces and is also more sensitive to smaller differences between energy levels. This kind of experiment can be studied in a fast and accurate way by IGC.

The energy heterogeneity is described either by the adsorption energy distribution or the adsorption potential distribution. The latter was used in this study since it was found to be less affected by experimental noise and to produce more reliable results. A good description of the calculation of adsorption energy distribution functions is given in the literature [4,5].

The adsorption potential distribution can easily be calculated from the sorption isotherm [1]. The isotherm is derived from an IGC pulse or frontal measurement by a variation of the probe molecule concentration. In this case, the retention time t_c obtained is converted into the retention volume V_N (Eq. (1)):

$$V_N = jw/m(t_c - t_0)T_C/273 \quad (1)$$

where t_0 is the deadtime, j the pressure drop correction, m the sample mass, w the flow-rate and T_C the column temperature.

The height h of the peak is converted into the partial pressure p (Eq. 2):

$$p = \frac{hV_{\text{loop}}P_{\text{sat}}273}{FwT_{\text{loop}}} \quad (2)$$

In Eq. (2) F is the area under the peak, p_{sat} the saturation pressure of the gas probe molecule, T_{loop} the loop temperature and V_{loop} the volume of the gas probe loop. This equation is slightly different from

the “standard” equation found in the literature due to the different flow control design in the used instrument.

The retention volumes and partial pressures can either be obtained from the maxima of peaks at different concentrations (peak maximum method) or from the tailing of a high concentration peak (elution by a characteristic point, ECP method). Graphical or numerical integration provides the isotherm in either case. A detailed description of this calculation procedure is given in Ref. [6].

In order to obtain the distribution function the partial pressures are converted into the adsorption potential A according to Eq. (3)

$$A = RT_C \ln\left(\frac{p_0}{p}\right) \quad (3)$$

where p is the partial pressure, p_0 the saturation pressure, R the gas constant and T_C the column temperature.

The distribution parameter Φ represents the first derivation of the sorbed amount n with the adsorption potential A (Eq. (4)).

$$\Phi = -\frac{dn}{dA} \quad (4)$$

The original equation included another division by the monolayer capacity to normalise the equation. However, this was not done in this application since more recent research shows that especially polar probe molecules do not necessarily form a monolayer on the surface [7].

3. Experimental

Two types of graphites have been investigated: an electro-graphite, supplied by Richard-Anton (Munich, Germany; E-graphite) and high purity synthetic graphite (Thermocarb TC-300), supplied by Conoco (Ponca City, OK, USA).

For both samples the sorption isotherms have been determined. All sorption experiments were carried out on an SMS-iGC 2000 (Surface Measurement Systems, London, UK). The materials were packed

into standard columns (30 cm×0.2 cm I.D.). Measurements were performed with *n*-hexane (dispersive probe) and polar probe molecules (ethanol and acetone), all supplied by Aldrich (Gillingham, UK). Prior to the measurements a pre-treatment was carried out for 2 h at 413 K to remove impurities adsorbed on the surface. After the pre-treatment procedure pulse injections were performed by a 0.25-ml gas loop at 303 K. For a peak maximum experiment measurements were undertaken at 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 0.95 p/p_0 . Calculations were performed using the SMS Analysis Software v1.2.

4. Results

Fig. 1 shows the pulse isotherms for a multiple injection experiment (Peak Maximum) with hexane on Thermocarb at 303 K.

The isotherms show different adsorption behaviour of the probe molecules on the same material. Although uptakes are fairly similar in the considered partial pressure range, hexane and acetone each show a type II isotherm while ethanol adsorbs as type III due to its different adsorption mechanism. For a type II isotherm the heat of sorption is much bigger than the heat of condensation while for type III the heat of sorption is only slightly higher or similar to the heat of condensation. The latter is typical for very polar probe molecules such as ethanol or water. The strong

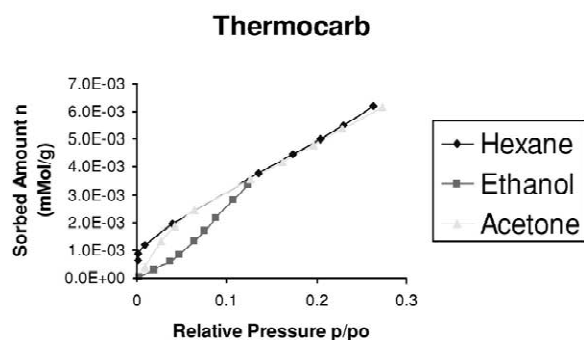


Fig. 1. Peak maximum isotherms of hexane, ethanol and acetone on Thermocarb at 303 K.

intermolecular interaction results in a high heat of condensation compared to the heat of sorption. This means that probe molecules tend to form clusters.

This is different for non-polar probe molecules such as hexane. Their intermolecular interaction is rather weak as it is only determined by induced dipoles. For this reason monolayer formation occurs.

This behaviour makes alkanes good probe molecules for the determination of properties such as the surface area. The surface area for Thermocarb was determined according to the BET model. This procedure is explained in detail elsewhere [6]. The surface area of Thermocarb was determined as 2.3 m²/g.

Adsorption potential distribution functions were calculated from the isotherms as described above. Fig. 2 shows a comparison of the (chemical) heterogeneity profiles of Thermocarb.

Potential distributions for hexane were calculated using both the ECP and peak maximum method. It can be seen that there is a good coincidence of the profiles obtained from each method.

Hexane shows two significant peaks while each of the polar probes show only one maximum in the adsorption potential range considered. The first maximum of hexane and the maximum of acetone seem to be located at similar adsorption potentials and represent, therefore, interaction with the same energy sites. The ethanol peak is shifted to higher adsorption potentials. This suggests an interaction with higher energy sites. Additionally, some hexane molecules seem to occupy even higher energy sites.

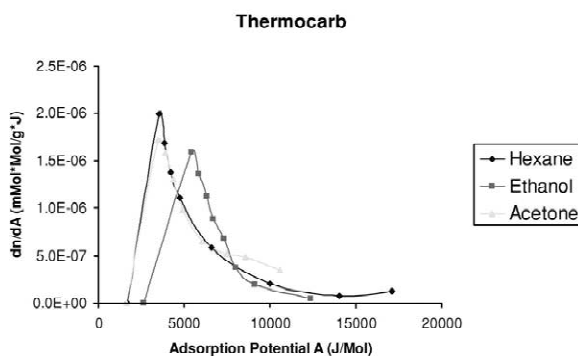


Fig. 2. Heterogeneity profiles of Thermocarb at 303 K for hexane, acetone and ethanol.

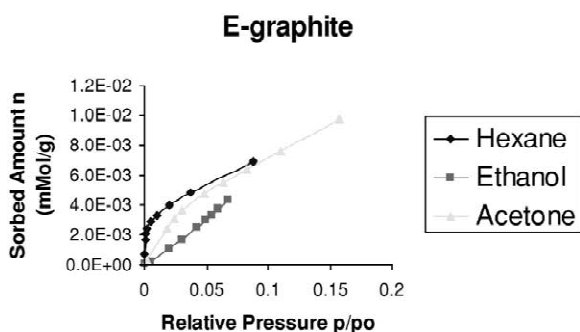


Fig. 3. Peak maximum isotherms of hexane, ethanol and acetone on E-graphite at 303 K.

The area under the curve is related to the uptake of the different energy sites, which demonstrates that the lower energy sites of Thermocarb have a bigger population than the high-energy sites.

Fig. 3 shows a comparison of the isotherms of the same probe molecules for E-graphite.

The isotherms indicate similar probe behaviour to that for the Thermocarb sample. Hexane and acetone show type II behaviour while ethanol adsorbs through a type III mechanism. The uptake for all three probe molecules, however, is significantly higher, which is expressed in the surface area of 3.2 m²/g.

The surface heterogeneity profiles are plotted in Fig. 4. It is obvious that the potential distributions are different from the distribution for Thermocarb. The results are compared in Table 1.

For E-graphite all peaks have shifted to higher energy levels. Ethanol is again occupying higher

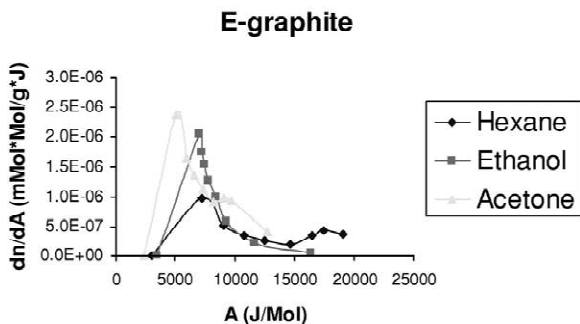


Fig. 4. Heterogeneity profiles of E-graphite at 303 K for hexane, acetone and ethanol.

Table 1

Adsorption potential distribution maxima for hexane, ethanol, acetone and surface areas (S_{BET}) of the graphite samples

| | Thermocarb | E-graphite |
|--------------------------------------|-------------------|-------------------|
| Hexane (kJ/mol) | 3.7 and 17.6 | 7.2 and 17.4 |
| Acetone (kJ/mol) | 3.6 | 5.1 and 9.1 |
| Ethanol (kJ/mol) | 5.4 | 7.0 |
| S_{BET} (m ² /g) | 2.3 (± 0.2) | 3.2 (± 0.2) |

energy sites and hexane has two significant peak maxima, similar to ThermocarbTM. Hexane, however, indicated a higher energy level than acetone for this material. Additionally, two peaks can be observed for acetone in the pressure range considered.

This shows that the E-graphite appears to be a material with a more highly energetic surface than Thermocarb. E-graphite also appears to be the more heterogeneous material as it shows for acetone an additional second peak. This is confirmed by the fact that both materials are manufactured using different processes. Thermocarb is a highly pure synthetic graphite and is used as conductive filler, while the E-graphite is a side product of an electrolytic process and therefore not expected to be of high purity.

Nevertheless, it is interesting to notice that the second hexane peak for both materials is located at the same energy level. This was also found for other graphite-based materials. Papirer et al. [8] found two, and in some cases even three significant maxima in the energy distribution for graphite materials and carbon blacks using heptane as the probe molecule. They associated the first peak with graphene layers. The second population was attributed to adsorption sites located on lateral surfaces. Occasionally occurring species with a maximum at an intermediate energy level was explained by the existence of certain polar surface groups. A quantitative comparison with the current study is difficult since a different calculation method has been applied which causes an offset, especially on the x -axis. However, the fundamental information given by the distribution function remains unchanged.

5. Conclusion

Adsorption potential distribution functions of hex-

ane, acetone and ethanol on two different graphites have been studied by IGC. Unlike nitrogen adsorption at 77 K, a study of heterogeneous surfaces at ambient temperature with a variety of polar and non-polar probe molecules allows more accurate and practically relevant conclusions to be drawn. IGC was proven as a useful tool as it makes a fast determination of low concentration sorption isotherms possible.

The different probe molecules show different sorption behaviour. Hexane and acetone represent a type II adsorption while ethanol shows a type III mechanism. The heterogeneity profiles for the different probe molecules on the two graphite samples are significantly different, particularly in the case of acetone. This may help to understand interaction processes in blends in more detail and can therefore provide parameters for quality control.

Acknowledgements

The authors would like to gratefully acknowledge

Conoco Inc. for supplying the Thermocarb samples used in this study.

References

- [1] M. Jaroniec, K. Gadkaree, J. Choma, *Colloids Surfaces A* 118 (1996) 203.
- [2] V. Choudhary, D. Akolekar, *J. Mol. Catal.* 60 (1990) 173.
- [3] F. Thielmann, E. Baumgarten, *J. Coll. Interf. Sci.* 229 (2000) 418.
- [4] H. Balard, *Langmuir* 13 (1997) 1260.
- [5] W. Rudzinski, D. Everett, in: *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, San Diego, CA, 1992.
- [6] J. Condor, C. Young, in: *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, 1979.
- [7] F. Thielmann, D. Burnett (in preparation).
- [8] E. Papirer, E. Brendle, F. Ozil, H. Balard, *Carbon* 37 (1999) 1265.