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iGC SEA Application Note 222

The Determination of Surface Adsorption Potential Heterogeneity Profiles on Graphite by Inverse Gas Chromatography

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In the present paper the adsorption potential distribution of two different graphite samples has been determined by Inverse Gas Chromatography (IGC SEA). This distribution function reflects the energetic heterogeneity profile of a surface and provides therefore interesting information on the nature and population of different surface sites. In this study IGC SEA is shown to be a fast and accurate technique for the determination of these energy distribution functions.

Introduction

There exist two types of surface heterogeneity: structural and energetic [1]. 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.
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.
In this study the surface energy distribution 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 porosity effects.

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 are strong acid-base interactions between surfaces and probe molecules or high adsorption potentials due to microporosity [2,3].

The pressure dependence, however, is a more appropriate method 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 SEA.

The energy heterogeneity is described either by the adsorption *energy* distribution or the adsorption *potential* distribution. The latter one 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. The isotherm is derived from an IGC SEA pulse or frontal measurement by a variation of the probe molecule concentration. In this case, the retention time obtained is converted into the retention volume and the height of the peak/front into the partial pressure. 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 [6].

In order to obtain the energy distribution function the partial pressures are converted into the adsorption potential *A* according to Equation 1:

$$A = R \cdot T \cdot \ln\left(\frac{po}{p}\right) \qquad (1),$$

where *p* is the partial pressure, *po* the saturation pressure, *R* the gas constant and *T* the column temperature.

The distribution parameter *Φ* represents the first derivation of the sorbed amount *n* with the adsorption potential *A* (Equation 2).

$$\Phi = -\frac{dn}{dA} \qquad (2)$$

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].

Method

Two types of graphites have been investigated: an electro-graphite, supplied by Richard-Anton KG (E-graphite) and high purity synthetic graphite (Thermocarb™ TC-300), supplied by Conoco Inc.

For both samples the isotherms have been determined. All sorption experiments were carried out on an SMS-iGC 2000. The materials were packed into standard columns (0.2 cm ID, 30 cm in length). Measurements were performed with hexane (dispersive probe) and polar probe molecules (ethanol and acetone), all supplied by Aldrich. 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/po. Calculations were performed using the iGC Standard Analysis Software and the Advanced Analysis Software v1.2.

Results

Figure 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 intermolecular interaction results in a high heat of condensation compared to the heat of sorption.

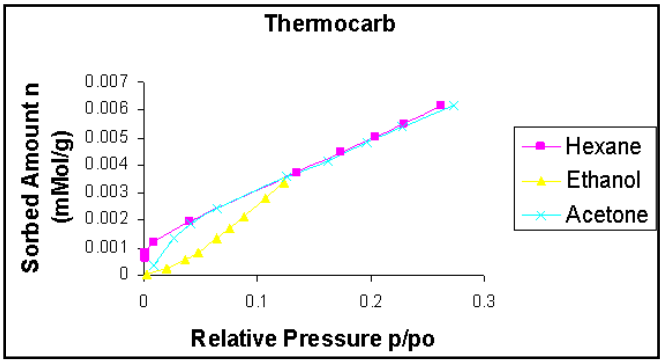

Figure 1. Peak Maximum isotherms of hexane, ethanol and acetone on Thermocarb™.

This is different for non-polar probe molecules such as hexane. Their intermolecular interaction is rather weak as it is only dominated by induced dipoles.

This behaviour makes alkanes good probe molecules for the determination of "dispersive" 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 m^2/g.

Adsorption potential distribution functions were calculated from the isotherms as described above. Figure 2 shows a comparison of the heterogeneity profiles of Thermocarb™.

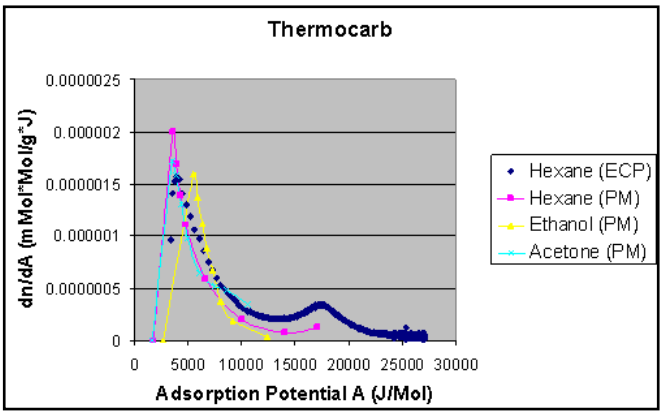

Figure 2. Adsorption potential heterogeneity profiles of Thermocarb™ at 303 K for hexane, acetone and ethanol.

Distributions for hexane were calculated for both ECP and Peak Maximum method. It can be seen that there is a good coincidence of the profiles obtained from both methods.

Hexane shows two distinct peaks while 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 might represent the interation with the same or similar 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 (second peak). The area under the curve is related to the uptake of the different energy sites. For the interaction of hexane the lower energy sites of Thermocarb™ have a bigger population than the high-energy sites.

Figure 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 m^2/g.

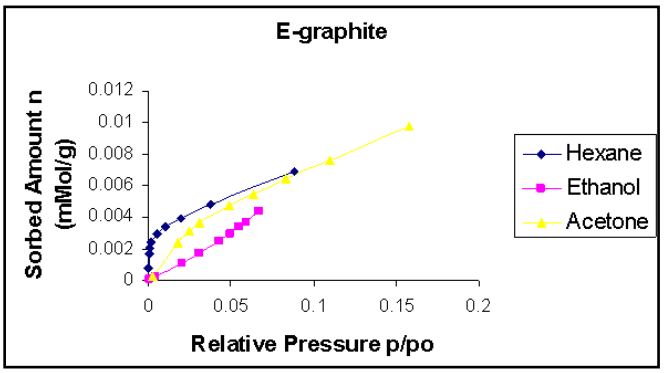

Figure 3. Peak Maximum isotherms of hexane, ethanol and acetone on E-graphite at 303 K.

The surface heterogeneity profiles are plotted in Figure 4.

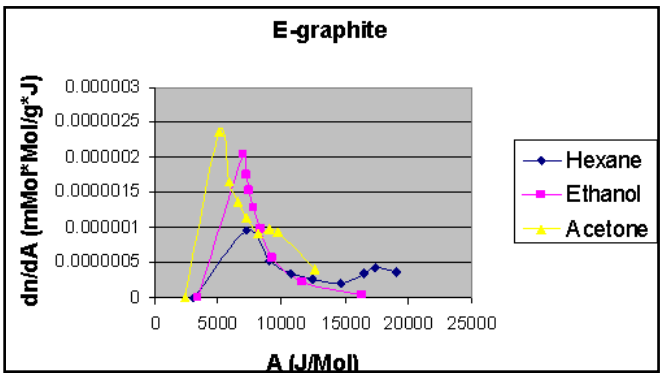

Figure 4. Adsorption potential heterogeneity profiles of E-graphite at 303 K for hexane, acetone and ethanol.

It is obvious that the adsorption potential distribution is different from the distribution for Thermocarb™. The results are compared in Table 1.

Table 1. Adsorption potential distribution maxima and surface areas 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)

For E-graphite all peaks have shifted to higher energy levels. Ethanol is again occupying the highest energy sites and hexane has two distinct peak maxima, similar to Thermocarb™. Hexane, however, indicated a higher energy level than acetone for this material. Additionally, two peaks can be observed for acetone in the considered pressure range.

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 comprises wider peaks and 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 [1] found two, and in some cases even three significant maxima in the energy distribution for graphite materials and carbon blacks. 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.

Conclusion

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

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.

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References

[1]Jaroniec, M., Gadkarec, K.P. and Choma, J., Colloid and Surfaces A 118 (1996), 203.
[2]Wesson, S., Proceedings of the SMS-IGC SEA Meeting, Princeton 1999.
[3]Thielmann, F. and Baumgarten, E., J. Coll. Interf. Sci. 229 (2000), 418.
[4]Balard, H., Langmuir 13 (1997), 1260.
[5]Rudzinski, W. and Everett, D.H., Adsorption of Gases on Heterogeneous Surfaces,
Academic Press, San Diego 1992.
[6]Thielmann, F. and Florian, I., SMS Application Note 208 (2002).
[7]Thielmann, F. and Burnett, D.J., SMS Application Note 26 (2005).
[8]Papirer, E. et al, Carbon 37 (1999), 1265.

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