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iGC SEA
Application
Note 213

Determination of Thermodynamic Parameters by Frontal Inverse Gas Chromatography at Infinite Dilution

Surface Measurement Systems Ltd.

Strongly adsorbing materials are sometimes difficult to measure by pulse IGC SEA since peaks become very broad and flat at infinite dilution conditions. An increase in temperature or concentration could change the surface thermodynamics significantly. An alternative method is the application of the frontal method at infinite dilution. This was until now difficult to realise since advanced instrumentation is required. This paper describes frontal measurements using the SMS-iGC SEA at low concentration and temperature. The heat of sorption on carbon blacks is determined as an example for a typical infinite dilution property.

Introduction

Inverse Gas Chromatography (IGC SEA) is a versatile tool for the measurement of energetic parameters. The measurements are usually carried out in the infinite dilution range. This range represents the linear part of the sorption isotherm (Henry region). In this region the uptake is independent of the surface coverage and interaction takes place only between the probe molecule and high energy adsorption sites. This fact leads to a high sensitivity of parameters measured in the infinite dilution range. These parameters are typically heat of sorption, surface energy and free energy or entropy [ ]. Since measurements can be carried out with both non-polar and acid-base components, the obtained parameters can be used to characterise the surface chemistry and also to measure the magnitude of the interactions.

Typically, these experiments are performed using a discontinuous pulse method. Although pulse measurements have been used quite successfully they are limited to smaller surface area materials or higher measurement temperatures. This is due to the fact that peaks for low injection concentrations at infinite dilution are very small and broad and therefore difficult to analyse. This problem cannot always be solved satisfactorily by using higher temperatures since the heat of sorption is different or, in some cases, reaction between the adsorbent and the probe molecule occurs.

An alternative is the use of frontal measurements. Such a continuous experiment can provide a well-defined breakthrough curve, even at small concentrations and low temperatures. The method was only applied in the past at finite dilution since accurate control of a low vapour concentration is experimentally difficult to realise. With modern flow control technology, the frontal method can be used for the determination of thermodynamic parameters at infinite dilution.

In the current paper heat of sorption measurements have been carried out on carbon black to check the feasibility of the frontal method.

Theory

IGC SEA methods can be divided into pulse and frontal measurements. Pulse methods are

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discontinuous and involve an injection of a certain amount of a vapour into the carrier gas stream. The adsorptive is transported by the carrier gas to the adsorbent in the column. In the ideal case an equilibrium state is reached. The adsorbed substance will then be eluted by the following carrier gas and the detector of the GC can detect this elution as a peak. In a frontal experiment the probe molecule is continuously added to the carrier gas stream. Therefore, a breakthrough curve is obtained rather than a peak. The retention time of a pulse experiment can be obtained from the peak maximum or the center of mass. These two should be very similar for an infinite dilution measurement since the peak is generally symmetrical in this region. For a frontal experiment, the retention time can be obtained from the turning point. In both cases the net retention volumes VN are computed using Equation 1.

T is the column temperature, m is the sample mass, F is the exit flow rate at 1 atm and 273.15K, t_R is the retention time for the adsorbing probe, t0 is the mobile phase hold-up time (dead time) and *j* is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed.

$$V_N = j \cdot F / m \cdot (t_R - t_0) \frac{T}{273.15} \qquad (1)$$

By varying the temperature in an IGC SEA experiment, a change in the retention volume can be observed. This relationship is used for the calculation of the heat of sorption. In the Henry's Law region the net retention volume is related to the differential heat of sorption *Δ*H by Equation 2,

$$\ln V_N / T = -\Delta H_A / RT + C \qquad (2)$$

where it is assumed that the sorption enthalpy is constant over a wide temperature range.

Under these conditions the heat of sorption is obtained from a plot of ln V_N/T versus 1/T [1].

Method

Carbon black N115 was supplied by Cabot, Boston, USA and heptane by Aldrich, UK. The sample was packed into a silanized glass column (30 cm long, 2 mm ID) without prior solvent extraction. A pre-treatment was carried out at 403 K for 5 hours in situ. All measurements were performed using the SMS-*iGC* 2000 system with the SMS Control Software v1.5. The sample was measured between 311.5 and 317 K and between 385 and 397 K in both pulse and frontal mode with a carrier gas flow rate of 15 ml/min.

For a pulse experiment heptane was injected in a concentration of 0.03 P/P0 via a loop with 0.25 ml volume. The obtained peaks showed a symmetrical shape, which confirmed infinite dilution conditions. The dead time was determined by a methane injection of 0.2 P/P0.

In the frontal experiment the heptane concentration was ramped from 0 to 0.03 P/P0 and then back to 0. Methane was ramped from 0 to 0.1 P/P0 and back to 0.

The heats of sorption calculations were performed by using the IGC Standard Analysis Macros v1.11.

Results

Figure 1 shows a set of (frontal) adsorption breakthrough curves measured between 311.5 and 317 K and a plateau concentration of 0.03 P/P_0. It can be clearly seen that the turning point is moving to smaller retention times with increasing temperature.

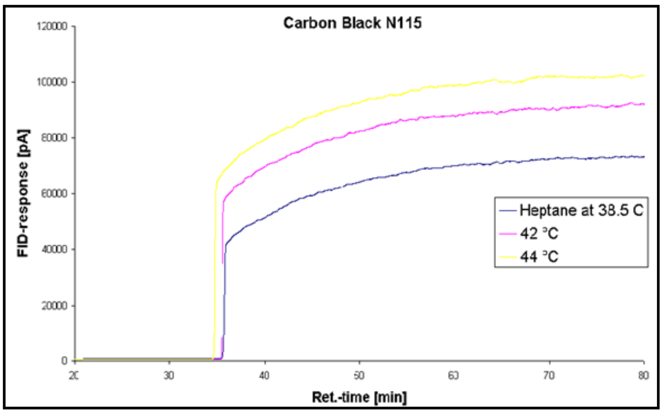

Figure 1. Breakthrough curves for heptane on carbon black N115. Measurements were carried out at infinite dilution in a frontal experiment between 311.5 and 317 K.

Figure 2 shows a typical heat of sorption plot by means of a heptane measurement on carbon black N115.

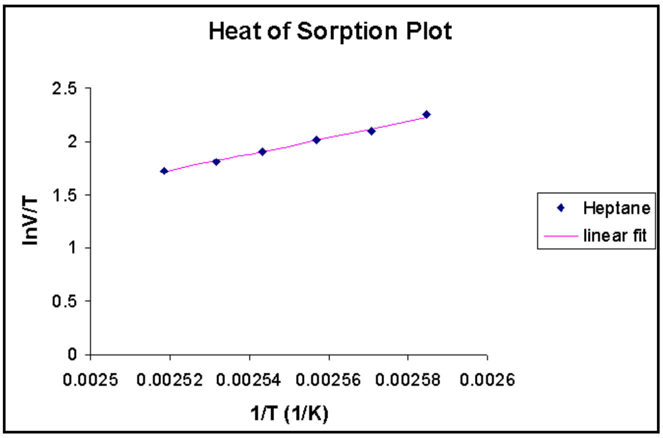

Figure 2. Heat of sorption plot of heptane on carbon black N115. Measurements were carried out at infinite dilution in a pulse experiment between 385 and 397 K.

The result for the pulse experiment at high temperatures was 64.58 kJ/Mol. At low temperatures no peak could be identified as expected due to the widening of the pulse. For the frontal experiment the heat of sorption was 70.29 kJ/Mol in the low temperature range, whereas at high temperatures no reliable measurement could be obtained. This was initially surprising since the frontal method was expected to deliver even more accurate results due to the continuous equilibrium conditions. However, this appears to be a technical problem since the accurate determination of the turning point is more difficult than the peak maximum. This doesn't affect the accuracy of the low temperature experiment due to the long retention times and the large differences in the retention volumes. For shorter retention times, however, the inaccuracy becomes more significant and the method less reliable. This problem can be solved by improving the raw data analysis. Therefore, a comparison of the pulse and frontal value should be put off until more accurate data are available.

A comparison with literature data is difficult since no values are published for N115. Therefore, we compared the results with literature data measured on N110, which should have similar energetic properties. Wang and Wolff [ ] have reported a value of 78.8 kJ/Mol, measured in a temperature range between 423 and 483 K. This value is much higher than the numbers measured here considering the fact that even N220 has a value 74.4 kJ/Mol. These differences may be due to different pre-treatment procedures. Firstly, no solvent extraction has been carried out in this study and secondly, a less drastic conditioning temperature has been applied.

However, the values are in a similar range as literature values. More materials with well-known surface properties must be investigated to confirm the capability of the frontal method at infinite dilution.

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Conclusion

Frontal IGC SEA at infinite dilution was introduced as a method for the measurement of energetic surface properties on carbon and other materials with high uptakes. The frontal method provides benefits compared to the usual pulse IGC SEA experiment in the characterisation of substances with a considerable high surface area at low temperatures and low concentrations. Although further improvements in the accuracy of the experimental method are necessary the potential as a useful tool in the determination of thermodynamic properties of strong adsorbing materials could be proven.

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References

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