



Heat of sorption studies on microcrystalline cellulose by pulse inverse gas chromatography at infinite dilution

Surface Measurement Systems Ltd

Inverse gas chromatography provides a fast and accurate method to measure the heat of sorption over different concentration and temperature ranges. Moreover iGC SEA also allows the study of this parameter at different relative humidities. This paper describes the determination of the heat of desorption of octane on microcrystalline cellulose at infinite dilution and two different humidities.

Introduction

The heat of sorption is a direct measure of the strength of interaction between the surface of a solid and gas molecules adsorbed on the surface. This parameter is usually obtained through a sorption isotherm measurement at high concentration. In this case it can be calculated either by the Clausius-Clapeyron equation or through the C-constant of a BET fit.

iGC SEA provides a fast and easy way to compute heat of sorption values directly from the retention volume at any concentration. At infinite dilution, iGC SEA is the only reliable method available since it requires no extrapolation of data [1].

In the current study microcrystalline cellulose is used as an adsorbent. Apart from its use in paper industry this material is a common ingredient in various pharmaceutical and food products. This paper shows the application of iGC SEA to determine the heat of desorption of octane on microcrystalline cellulose at two different relative humidities.

Theory

Heat of sorption experiments are carried out at infinite dilution. In this experiment a small amount of an organic vapour is injected into a carrier gas stream. At infinite dilution the adsorption is independent of the surface coverage of the adsorbed molecules. The result is a linear adsorption isotherm, which can be described by Henry's Law. In this case the experimental obtained peaks are symmetrical (Gaussian) and the retention time from the peak maximum can be used to calculate the retention volume. The net retention volumes V_R^0 are computed using Equation 1.

$$V_R^0 = j / m \cdot F \cdot (t_R - t_0) \cdot \frac{T}{273.15} \quad (1),$$

where T is the column temperature, m is the mass of the sample, F is the exit flow rate at 1 atm and 273.15K, t_R is the retention time for the adsorbing probe and t_0 is the mobile phase hold-up time (dead time). j is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed.



$$j = \frac{3}{2} \left[\frac{\left(\frac{P_i}{P_0} \right)^2 - 1}{\left(\frac{P_i}{P_0} \right)^3 - 1} \right] \quad (2)$$

In the Henry's Law region the net retention volume is related to the differential heat of sorption by Equation 3.

$$\ln V_N / T = -\Delta H_A / RT + C \quad (3)$$

where it is assumed that the adsorption enthalpy is independent of temperature. Under these conditions the heat of sorption can be obtained from a plot of $\ln V_N / T$ versus $1/T$ [2].

Method

Empty iGC SEA columns (SMS standard column with 2mm ID and 30 cm length) were packed with microcrystalline cellulose (MCC), Avicel PH-101. All the sorption experiments were carried out on an SMS-iGC 2000. Measurements were done with octane between 302 and 316 K at 0 % and 50 % RH. Before measurements a pretreatment was carried out for 10 hours at the initial temperature and relative humidity.

Results

Figure 1 shows the heat of sorption plot for 0 % and 50 % RH measured with octane between 30° and 46 °C on a typical column packed with MCC.

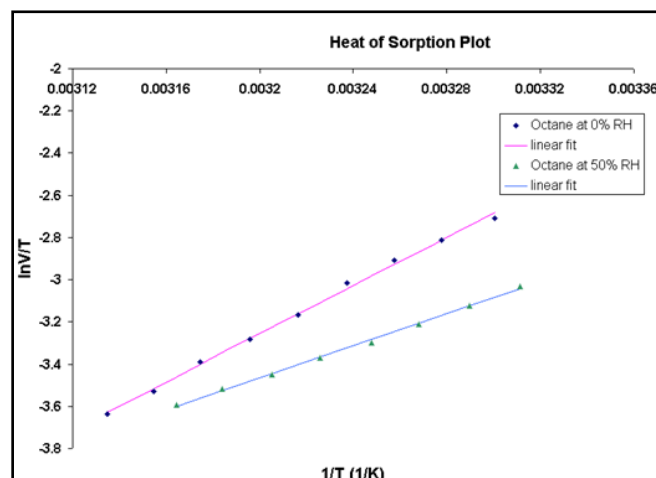


Figure 1. Heat of sorption plot and linear fits for an octane measurement on MCC between 30° and 46 °C at 0 % and 50 %.

The calculation of the heat of sorption values was done with the iGC Analysis software version 1.1. The average value for a series of measurements at 0% RH is 47.77 kJ/Mol and at 50% RH 32.90 kJ/Mol.

The drop in the heat of desorption with increasing relative humidity agrees with the trend observed by Katz and Gray [3] for surface energy measurements at different relative humidities on cellophane. They obtained a constant surface energy at low RH whereas at high RH the values were significantly smaller.

This effect may be caused by a formation of water clusters on the surface rather than by a formation of a monolayer. The cluster would still allow an interaction between the alkane probe molecules and the dispersive centres on the surface. At very high RH the cluster would become so large that the dispersive interaction is hindered and the surface energy as well as the heat of sorption would drop. This theory is supported by a comparison of the obtained values for the heat of desorption with the heat of condensation (38.58 kJ/Mol for octane).

Usually the heat of condensation is expected to be smaller than the heat of sorption. However, at high RH a significant amount of the solid surface is covered with water clusters and hence the

dominating interaction will be similar in magnitude to the heat of mixing for octane and water which is expected to be relatively small.



Conclusion

iGC SEA was demonstrated as a useful technique to measure the heat of sorption at different relative humidities. In combination with other data these measurements can even be used to obtain information about the nature of interaction between surface and adsorbate.

Acknowledgement:

Surface Measurement Systems thank Frank Thielmann and David Butler for their contributions to the application note.

References

- [1] Kiselev, A.V. and Yashin, Y.A., *Gas Adsorption Chromatography*, Plenum, New York, 1969
- [2] Condor, J.R. and Young, C.L., *Physicochemical Measurement by Gas Chromatography*, John Wiley and Sons, Chichester, 1979.
- [3] Katz, S. and Gray, D.G., *Journal of Colloid and Interface Science* 82 (1981), 339/
- [4] CRC Handbook of Chemistry and Physics, 57th edition 1976, CRC Press, Cleveland.

Head Office:
Surface Measurement Systems, Ltd
5 Wharfside, Rosemont Road
London HA0 4PE, UK
Tel: +44 (0)20 8795 9400
Fax: +44 (0)20 8795 9401
Email: science@surfacemeasurementsystems.com

United States Office:
Surface Measurement Systems, Ltd, NA
2125 28th Street SW, Suite I
Allentown PA, 18103, USA
Tel: +1 610 798 8299
Fax: +1 610 798 0334

