

DETERMINING THE ISOSTERIC ENTHALPY OF ADSORPTION OF CO₂ ON ACTIVATED CARBON AT NEAR AMBIENT TEMPERATURE

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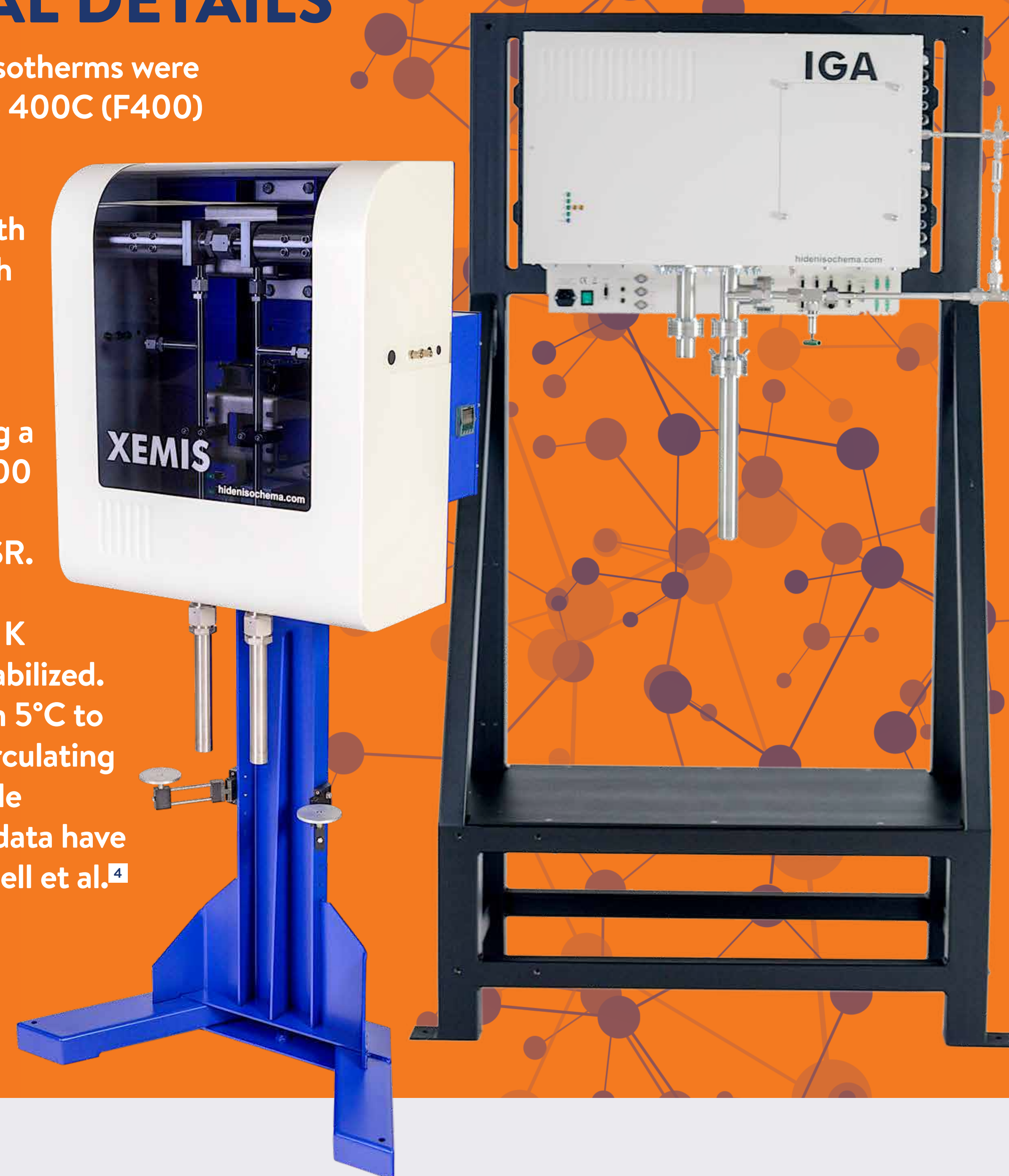
INTRODUCTION

The differential enthalpy of adsorption is an important thermodynamic parameter for characterizing porous adsorbents.^[1] It provides a measure of the strength of adsorption of any given adsorbate, but it is also required when modelling adsorbent columns for separation processes and other adsorption applications. Differential enthalpies of adsorption can be determined directly using adsorption calorimetry, but it is more common to extract the so-called isosteric enthalpy of adsorption, ΔH_{iso} – the differential molar enthalpy at constant surface coverage or loading – from gas or vapor adsorption isotherms measured at two or more closely spaced temperatures.^[2]

Accurate adsorption isotherm data are required for such an analysis; however, results can be affected by the manner in which experimental data are analyzed. There are several approaches. Data can be used directly or interpolated to extract the pressure at fixed (isosteric) uptake points for use in the van 't Hoff or Clausius-Clapeyron equations; isotherm equations can be fitted to data and the results of fits used to calculate ΔH_{iso} ; or a form of the virial equation can be fitted to multiple isotherms, resulting in ΔH_{iso} as a function of coverage or loading. Different results can be obtained by using these different methods. Here, we use high resolution CO₂ adsorption data for a commercial activated carbon, measured on two different gravimetric instruments, to calculate ΔH_{iso} as a function of loading using both the virial equation and interpolation.

EXPERIMENTAL DETAILS

Low pressure CO₂ adsorption isotherms were measured on Calgon Filtrasorb 400C (F400) activated carbon using an IGA-001 gravimetric gas sorption analyzer, equipped with a 1 bar pressure transducer with a quoted accuracy of $\pm 0.04\%$ of full scale range (FSR). High pressure CO₂ adsorption isotherms were measured using a XEMIS-001 equipped with a 200 bar pressure transducer with a quoted accuracy of $\pm 0.04\%$ FSR. Samples were degassed under high vacuum ($< 10^{-3}$ Pa) at 423 K until the sample weight had stabilized. Isotherms were measured from 5°C to 45°C in 5°C steps, using a recirculating waterbath to control the sample temperature. The XEMIS-001 data have been previously published by Bell et al.^[4]



THE VIRIAL EQUATION

Use of the virial-type thermal equation introduced by Czepirski and Jagiello^[3] allows isotherms measured at different temperatures to be fitted simultaneously, in order to calculate ΔH_{iso} from the parameters obtained from the fitting process.

The equation is given by,

$$\ln \frac{p}{n} = \sum_{i=0}^{m_1} c_i n^i + \frac{1}{RT} \sum_{i=0}^{m_2} d_i n^i$$

where p is pressure, n is the molar amount adsorbed on a mass basis, c_i and d_i are fitting parameters, m_1 and m_2 are the number of parameters in each term, T is temperature, and R is the universal gas constant.

The fitted parameters are then used to calculate ΔH_{iso} using the following expression,

$$\Delta H_{iso} = \sum_{i=0}^{m_2} d_i n^i$$

RESULTS AND DISCUSSION

Figure 1 shows the XEMIS-001 data for F400, previously reported by Bell et al.^[4] Uptake values are displayed as total or absolute adsorption, using the assumption that the adsorbed phase volume equals the estimated pore volume of 0.51 cm³ g⁻¹ for this material, while the real gas behaviour is represented as fugacity. Figure 2 shows the virial fits to the data shown in Figure 1, using two c parameters (c_1, c_2) and six d parameters ($d_1, \dots, d_6$). This number of parameters provides

excellent fits to the data. Figure 3 shows the calculated values of ΔH_{iso} using both the IGA-001 and XEMIS-001 data, interpolated using polynomials, and the same data fitted using the virial equation. Excellent agreement was found except for the virial equation data at the lowest uptakes, due to the lack of measurement resolution at very low pressures in the XEMIS-001 data.

Several conclusions can be drawn from this work. Both the virial approach using the equation of Czepirski and Jagiello^[3] and interpolation using a polynomial equation can be used to calculate consistent ΔH_{iso} values as a function of coverage; use of absolute (or total) adsorption and fugacity are required for high pressure CO₂ adsorption; and high resolution data are required to accurately determine ΔH_{iso} at low coverages.

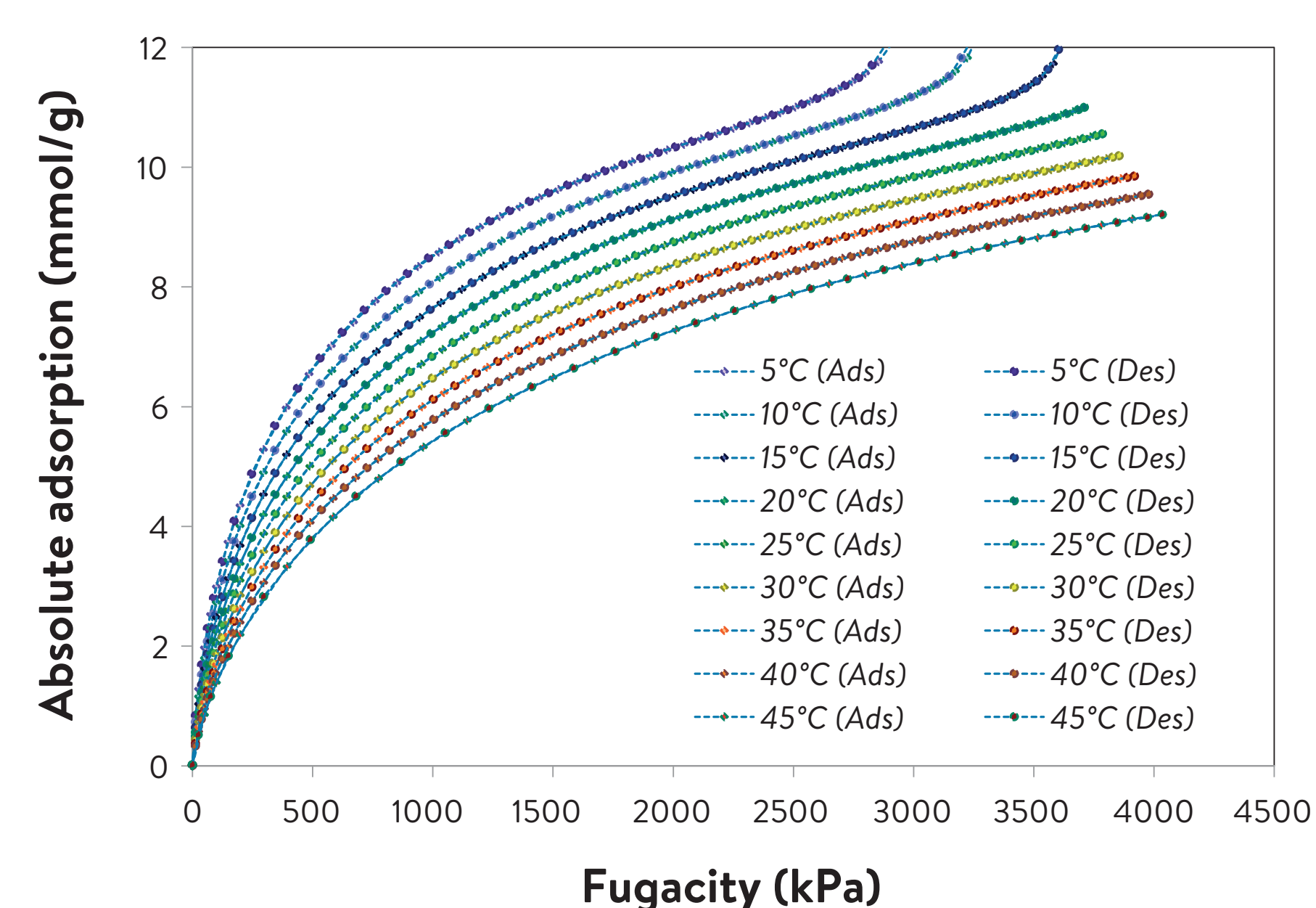


Figure 1: CO₂ adsorption isotherms for F400, measured on a XEMIS-001 in the temperature range 5°C to 45°C.^[4] In the legend, 'Ads' denotes adsorption, 'Des' denotes desorption.

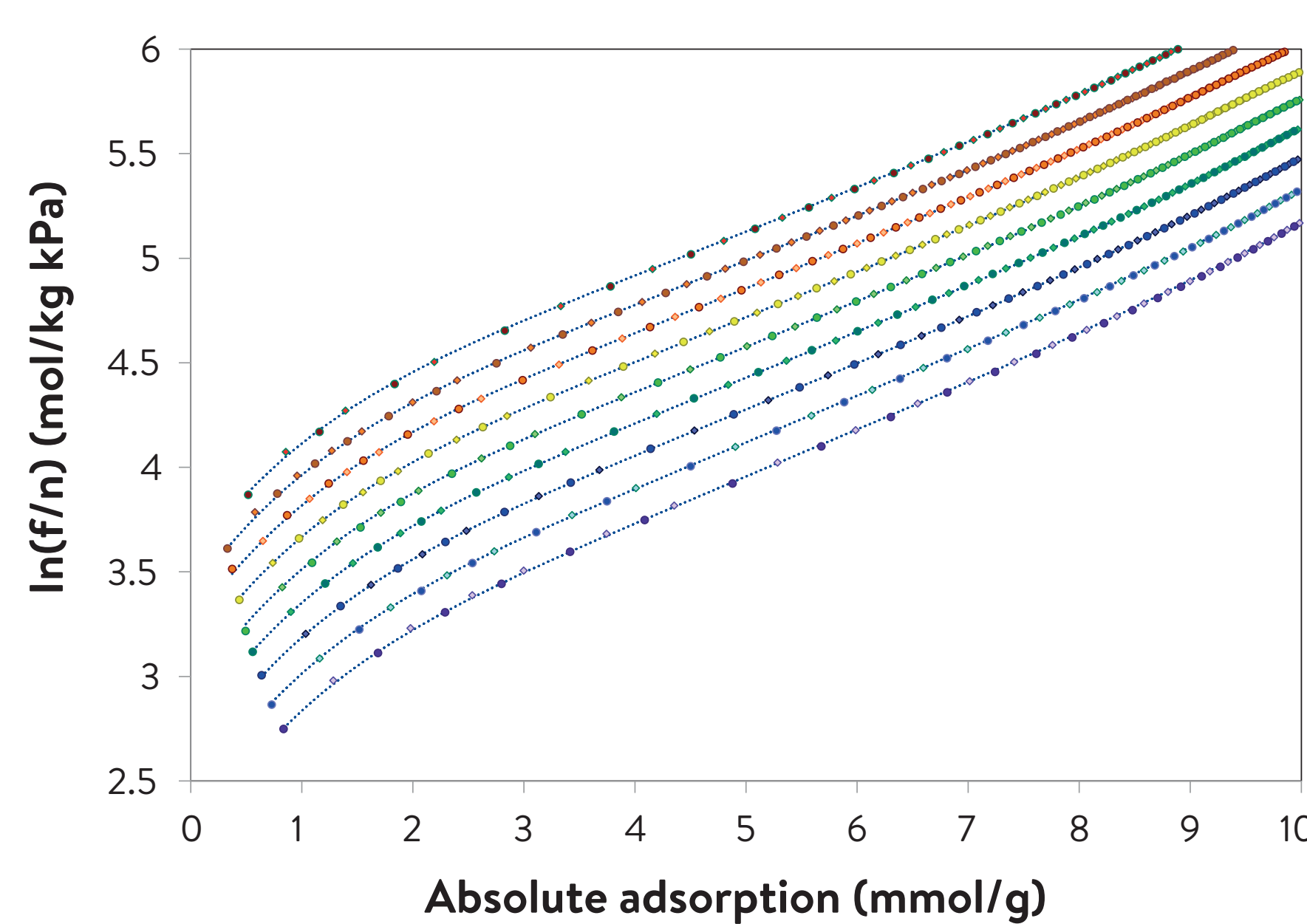


Figure 2: Fits to the virial equation for the data in Fig. 1, plotted as $\ln(f/n)$ vs absolute adsorption, where f is fugacity. The symbols are experimental data; lines are the virial plots.

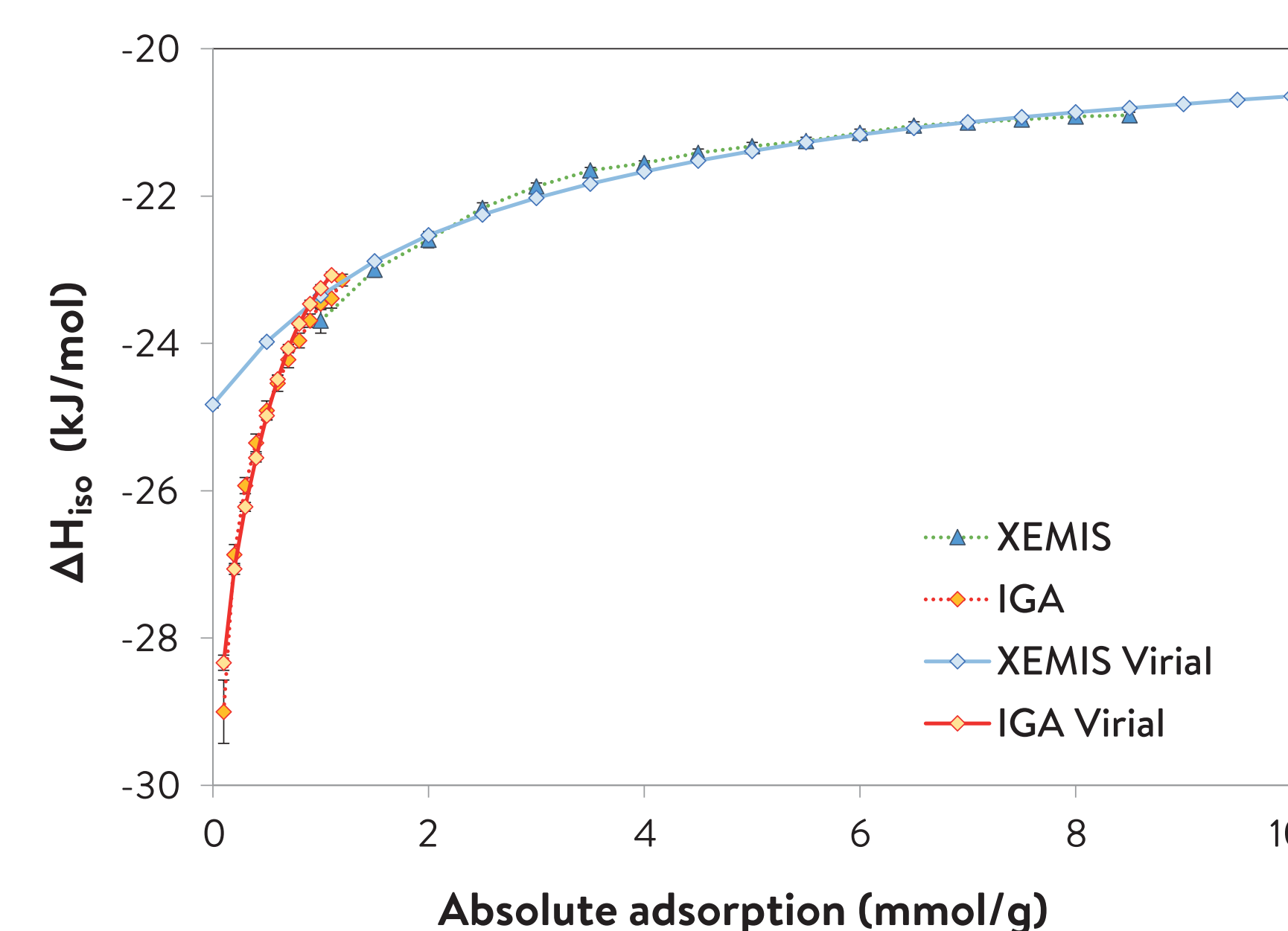


Figure 3: The isosteric enthalpy of adsorption of CO₂ on F400, calculated using polynomial interpolation and fits to the virial equation using both IGA and XEMIS-001 data.

SUMMARY

- ▶ The isosteric enthalpy of adsorption is an important thermodynamic parameter
- ▶ ΔH_{iso} can be reliably obtained using a virial equation and by interpolation using a polynomial
- ▶ This was demonstrated using CO₂ adsorption isotherms measured over a wide pressure range at near ambient temperatures on a commercial activated carbon
- ▶ Use of absolute adsorption and fugacity are required at elevated pressures to determine reliable values of ΔH_{iso}

REFERENCES

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