

High pressure methane adsorption by activated carbon: adsorption isotherms and isosteric enthalpy of adsorption*

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Introduction

There are many applications for gas adsorption by nanoporous materials, including gas separation, purification and storage [1]. The determination of the adsorption properties of a particular material, including absolute uptakes, as a function of temperature and pressure, and the enthalpy of adsorption as a function of surface coverage, is important in order to assess its suitability for any given application. For gas storage, in particular, high pressure measurements are required. The accurate determination of the absolute uptake is dependent upon the quality of the experimental data, but also on the assumptions used to convert the excess adsorption to absolute adsorption. Similarly, in order to analytically represent and interpolate data for the calculation of the isosteric enthalpy of adsorption, ΔH_{iso} , using van 't Hoff plots, it is necessary to select a suitable isotherm model.

In this application note we demonstrate the use of an IMI-HTP high pressure sorption analyzer to assess the Langmuir, Freundlich, Sips (Langmuir-Freundlich) and Tóth isotherm equations [2] for the description of the adsorption of methane by a commercial activated carbon up to pressures of approximately 6.5 MPa in the temperature range 307 – 329 K. We also use the data obtained using the Sips and Tóth expressions to calculate ΔH_{iso} as a function of surface coverage or methane uptake.

Isotherm Equations

The Langmuir equation describes the localized adsorption of a monolayer of atoms or molecules on a homogeneous surface in the absence of adsorbate-adsorbate interactions. It is given by,

$$\frac{n_a}{n_m} = \frac{bP}{1 + bP} \quad (1)$$

where n_a is the amount adsorbed and n_m is the monolayer capacity, so that the surface coverage, $\theta = n_a/n_m$, and P is the pressure. b is the adsorption coefficient, which is related exponentially to the positive value of the energy of adsorption.

The Freundlich equation is given by,

$$\theta = KP^{1/n} \quad (2)$$

where K and n are empirical parameters. The Freundlich equation was originally empirical in nature but it can also be derived using the multi-site Langmuir equation, by assuming an exponential adsorption site energy distribution.

The Langmuir-Freundlich isotherm is given by,

$$\frac{n_a}{n_m} = \frac{(kP)^{1/n}}{1 + (kP)^{1/n}} \quad (3)$$



Figure 1: The IMI-HTP high pressure sorption analysis instrument.

where k has the same meaning as b in the Langmuir equation, and n is considered a measure of the heterogeneity of the adsorbent. This equation was originally proposed as an empirical relation by Bradley [3], but was also later derived by Sips [4] assuming Langmuir isotherm behaviour and a near-Gaussian distribution of adsorption site energies.

The Tóth equation uses another exponent, t , to represent the heterogeneity, and is given by,

$$\frac{n_a}{n_m} = \frac{bP}{[1 + (bP)^t]^{1/t}} \quad (4)$$

where b and t are specific to a particular adsorbate-adsorbent system.

Experimental Details

All measurements were performed using a fully automated IMI-HTP manometric analyzer that can be used to determine the gas sorption properties of materials up to pressures of 20 MPa. Methane adsorption isotherms were determined using 1.755 g of Filtrasorb F-400, up to 6.5 MPa at temperatures of 307 K, 312 K, 316 K, 320 K, 325 K and 329 K. The volumes of the calibrated dosing manifold and the sample cell were 6.32 cm³ and 16.47 cm³, respectively. These volumes were determined by pycnometry, using helium as the calibration fluid. The temperature of the manifold was maintained constant at 308 K, with a stability of ± 0.1 K. The pressure was measured using a 10.0 MPa range transducer with an accuracy of $\pm 0.04\%$ of

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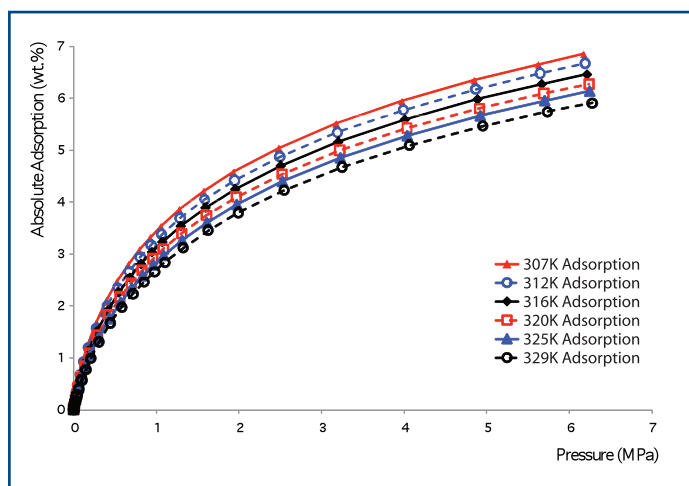


Figure 2: Absolute methane adsorption by 1.755 g activated carbon (Filtrisorb F-400) at temperatures between 307 K and 329 K.

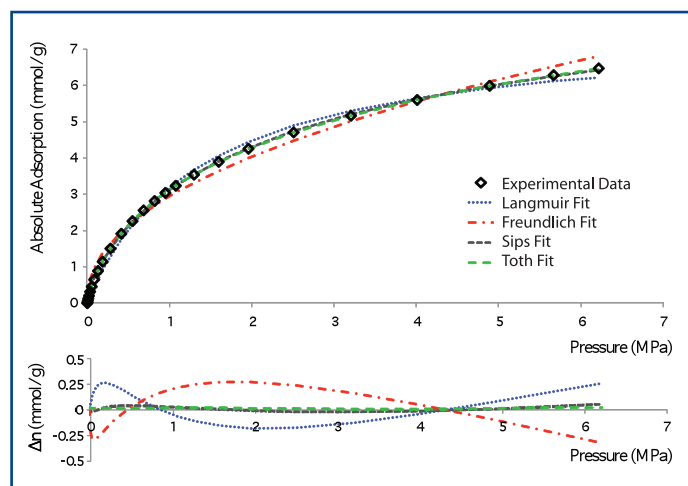


Figure 3: Langmuir (blue), Freundlich (red), Sips (grey) and Tóth (green) fits, top, and residuals, bottom, for absolute uptake data at 316 K.

full scale. The compressibility of methane was determined using a linear interpolation between tabulated compressibility values produced using the NIST REFPROP database [5]. For methane, the NIST database uses the equation of state of Setzmann and Wagner [6].

Results and Discussion

The excess uptake isotherms were recorded using the IMI-HTP and the data used to determine the corresponding absolute uptake isotherms, which are shown in Fig. 2. These were fitted using equations (1) to (4), and the isosteric enthalpies of adsorption were calculated from van 't Hoff plots constructed using the best fit parameters. Fig. 3 shows comparative data fits for absolute adsorption measured at 316 K, with the Tóth equation providing the best fit, as was found for all of the absolute adsorption isotherms in this study. For all excess adsorption isotherms, the Sips equation provided the best fit. The Sips and Tóth equations consistently provided significantly better fits than the Langmuir and Freundlich equations for both excess and absolute adsorption. Fig. 4

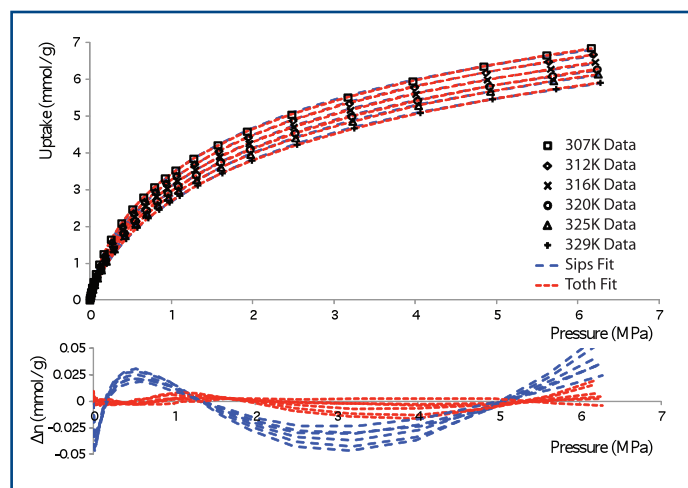
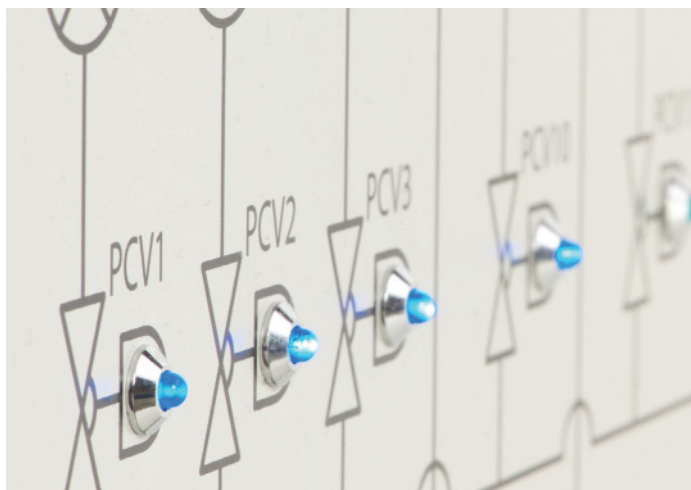


Figure 4: Sips (blue) and Tóth (red) fits, top, and residuals, bottom, for absolute uptake isotherms at temperatures between 307 K and 329 K

shows the Sips and Tóth equation fits for the absolute adsorption data throughout the measured temperature range.

The better fit provided by the Tóth equation, compared to the Sips equation, can be seen clearly in the residuals in the lower plot. Fig. 5 shows the Sips and Tóth equation fits for the excess adsorption data throughout the measured temperature range. It can be seen from the residuals in the lower plot of Fig. 5 that the Sips equation appears to provide a better overall fit than the Tóth equation; however, at low surface coverage, the magnitude of the residuals appears to be approximately equal.

Fig. 6 shows ΔH_{iso} as a function of coverage, calculated using the best fit parameters from the Sips and Tóth models and isotherm data recorded at different sets of temperatures. The values of ΔH_{iso} calculated in this study vary beyond the approximate 23 – 25 kJ mol⁻¹ range reported elsewhere for methane adsorbed onto activated carbons [7], although ΔH_{iso} is known to change as a function of both temperature and



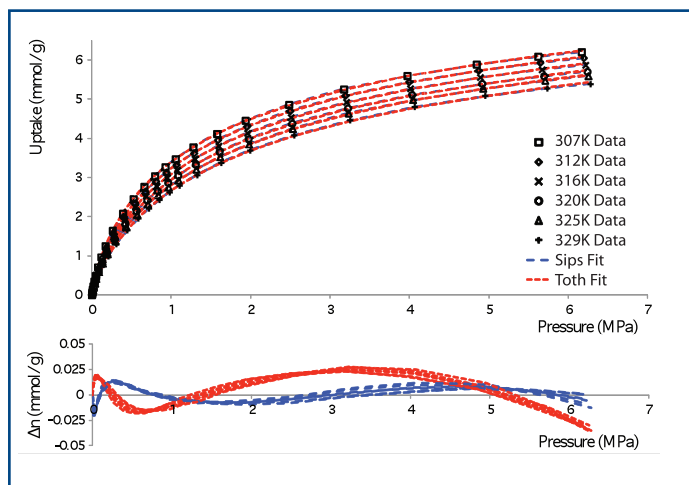


Figure 5: Sips (blue) and Tóth (red) fits, top, and residuals, bottom, for excess uptake isotherms at temperatures between 307 K and 329 K.

surface coverage [8]. No clear correlation between the calculated enthalpies and the isotherm temperatures or specific surface coverage was found, suggesting that the different trends seen in Fig. 6 are most likely due to the analysis methods rather than real physical effects. This demonstrates that different values of ΔH_{iso} may be calculated from the same experimental data, depending upon the choice of equation and the temperatures of the isotherms used to construct van 't Hoff plots. Similar results have been found recently for hydrogen adsorption by a number of porous materials [9]

Conclusions

The Tóth equation provided the best fit to all absolute adsorption isotherm data measured in this study, while the Sips equation best modelled the excess adsorption data. A wide range of ΔH_{iso} values were found using the same experimental data but different analysis methods, suggesting that ΔH_{iso} values calculated using any one single method

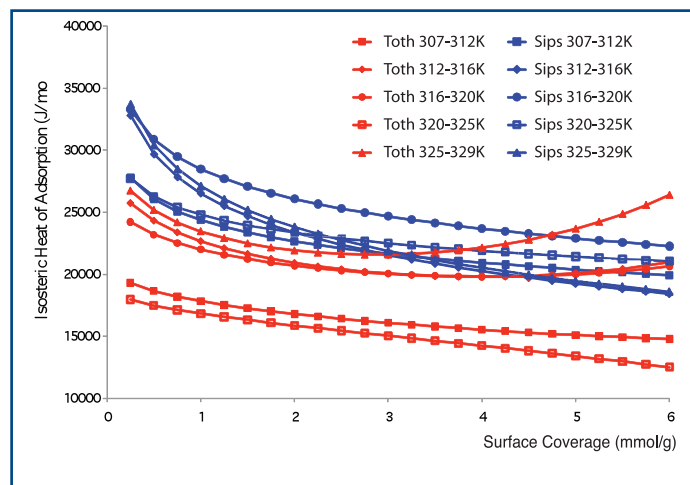


Figure 6: The isosteric enthalpies of adsorption for methane on F-400 carbon, calculated from various isotherms fitted using the Sips and Tóth equations.

could contain a large potential error. The significant effect that the choice of isotherm model and the selected data temperature range has on the calculated values of ΔH_{iso} suggests that single quoted ΔH_{iso} values should be treated with caution, and demonstrates the importance of clearly stating the method used when reporting isosteric enthalpies of adsorption. In addition, this application note has successfully demonstrated the use of an IMI-HTP analyser to determine the high pressure adsorption of methane by an activated carbon.

For more information, please email info@hidenisochema.com

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