BET and microporous materials – Upper limit?

‘Two-point BET’
Calculate C for two consecutive data points:

\[ y_{i} = \frac{1}{Cq_{m}} \left( \frac{C-1}{Cq_{m}} \right)_{i} \quad \xrightarrow{\text{transition}} \quad C_{i} = \frac{I_{i} + s_{i}}{I_{i}} \]

Transition determines upper \( p/p_0 \) limit
Easy implementation

\( \text{de Lange et al., Micropor Mesopor Materials 200 (2014) 199–215} \)

Linearized BET

2-point BET: upper limit
lower limit \( p/p_0 \)?
BET – How to apply to mesoporous materials?

**Studentized residuals**

Non-linear parameter estimation

maximize # data points

all data points

8 points removed

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γ-alumina ($N_{tot} = 0$)

γ-alumina ($N_{tot} = 1$)

γ-alumina ($N_{tot} = 3$)

γ-alumina ($N_{tot} = 5$)
BET analysis

2-point BET: upper limit $p/p_0$
Studentized residuals: lower limit

$S_{BET} = 185 \pm 5 \text{ m}^2/\text{g}$

$S_{BET} = 185.3 \pm 0.8 \text{ m}^2/\text{g}$

95% conf. level

BJH pore size distribution

Desorption

Adsorption

statistically highly doubtful
BJH pore size distribution

\[ \frac{V_{man}}{V_{cell}} = 2.21 \]

\[ \frac{V_{man}}{V_{cell}} = 1.35 \]

\[ \frac{V_{man}}{V_{cell}} = 1.06 \]

\[ \frac{V_{man}}{V_{cell}} = 0.69 \]

Literature example: MIL-101(Cr)

Recalculating \( S_{BET} \) and \( V_p \)

Recommendations $\text{N}_2$ adsorption @77 K

- Regarding isotherm measurement and pore volume
  - Use $2 \leq V_{\text{man}} / V_{\text{cell}} \leq 3$ (e.g., by using glass filler rods):
    - Minimal uncertainty
    - Less artificially enlarged desorption hysteresis

- Regarding BET surface area
  - Use direct fitting method (nonlinear parameter estimation)
  - Relative pressure
    - upper limit by two-point BET calculation
    - lower limit (mesoporous) Use residual distributions

- Regarding BJH-pore size distribution
  - Compare PSD from adsorption and desorption to check for artifacts
  - Do not apply below $p/p_0 = 0.42$ (desorption)
  - Interpret data only qualitatively

- When reporting
  - State exact determination procedure
  - Don't exaggerate accuracy (# significant digits)

Thank you for your attention