Adsorption of $C_1$–$C_7$ Normal Alkanes on BAX Activated Carbon. 1. Potential Theory Correlation and Adsorbent Characterization

Charles E. Holland, Shaheen A. Al-Muhtaseb, and James A. Ritter*

Department of Chemical Engineering, College of Engineering and Information Technology, Swearingen Engineering Center, University of South Carolina, Columbia, South Carolina 29208

Single-component adsorption equilibria of the n-alkane series $C_1$–$C_7$ on Westvaco BAX-1100 activated carbon were measured over very broad ranges of temperature and pressure, spanning 293–393 K and 0.06–4964 Torr, depending on the n-alkane. The 4278 data points were correlated successfully with potential theory and collapsed essentially into one characteristic curve. A useful functional form of the characteristic curve was also obtained. A new potential theory approach, based on a multisegment Gaussian distribution, qualitatively predicted both the pore size distribution and the total pore volume of the BAX-1100 activated carbon from the adsorption equilibria of the $C_3$–$C_7$ n-alkanes, with errors in the total pore volume ranging between 1 and 5%. This extensive data set should prove to be very useful for testing adsorbent characterization schemes, evaluating adsorption isotherm models, estimating adsorption thermodynamic properties of these systems, and modeling adsorption processes concerning hydrocarbon separations and purification, in general.

Introduction

The measurement of single-component adsorption equilibria over a relatively wide range of experimental conditions has many different uses. It is extremely useful for characterizing different adsorbent surfaces and investigating the nature of their interactions with the adsorbate molecules.1–4 It is also useful for evaluating the ability of different models to correlate the data over a wide range of conditions. Reliable correlations are also essential for estimating the dependence of different thermodynamic properties of the adsorbed phase on the adsorption conditions,1–9 and they are useful for simulating cyclic adsorption processes, such as temperature and pressure swing adsorption processes, because the process conditions vary widely during cycling.

However, single-component adsorption equilibria measured over wide ranges of pressure and temperature on commercially available adsorbents are quite rare in the literature. Much of the data that is available is either obsolete because the adsorbent is not being manufactured10–12 or measured over a relatively narrow range of experimental conditions with only a few data points obtained. For this reason, many of the models in the literature may not be reliable when extrapolated over a broad range of conditions, such as those encountered in cyclic adsorption processes. Therefore, the major objective of this work is to present an extensive set of single-component adsorption isotherm data that can be used for adsorbent characterization, model evaluation, thermodynamic property estimation, and process modeling.

In Part 1 of this series, the single-component adsorption equilibria for the n-alkane series $C_1$–$C_7$ measured on Westvaco BAX-1100 activated carbon over a wide range of conditions are presented, along with a characteristic curve predicted from potential theory. A new potential theory approach is also presented for predicting the pore size distribution (PSD) and the total pore volume of the BAX-1100 activated carbon from the adsorption equilibria of the $C_3$–$C_7$ n-alkanes, with errors in the total pore volume ranging between 1 and 5%. This extensive data set should prove to be very useful for testing adsorbent characterization schemes, evaluating adsorption isotherm models, estimating adsorption thermodynamic properties of these systems, and modeling adsorption processes concerning hydrocarbon separations and purification, in general.

Theory

The potential theory model has been used extensively for correlating adsorption equilibria on porous adsorbents.14–17 It has been most successful at unifying the adsorption equilibria for one adsorbent into a single characteristic curve that accounts for the effects of temperature and, when an empirical coalescing factor ($\beta$) is used,15 the polar interactions between the adsorbent and different adsorbates. One of the more common expressions for the characteristic curve is

$$nv = f\left(\frac{A}{\sqrt{v}}\right)$$

where the adsorption potential, $A$, is given by

$$A = RT \ln(P_r^{-1}) = RT \ln\left(\frac{P}{P_0}\right)$$

and $n$ is the amount adsorbed; $R$ is the universal gas constant; $T$ is the temperature; $P_r = (P/P_0)$ is the relative pressure; $P$ and $P_0$ are the equilibrium pressure and vapor pressure of the adsorbate, respectively, at temperature $T$; and $\beta$ is the coalescing factor. $v$, the molar volume of the adsorbed phase, has been estimated in
various ways in the literature.\textsuperscript{15,16} It is estimated here from the molar volume of the adsorbate in the liquid phase at its normal boiling point temperature. Other alternative forms of the adsorption potential have also been explored\textsuperscript{14–17} but are not considered here.

The potential theory has also been utilized for characterizing porous adsorbents\textsuperscript{18–20} and even for predicting pore size distributions.\textsuperscript{18,20–23} The most common and fundamental technique is based on the original form of Dubinin’s potential theory for microporous adsorbents\textsuperscript{18,20}

\[
W = W_0 \exp \left[ -\frac{2}{\beta E_0} \right] (3)
\]

where \(W\) is the total volume adsorbed (= \(nv\)), \(W_0\) is the total pore volume, \(E_0\) is the energy of adsorption, and \(A\) and \(\beta\) are as previously defined. An empirical dependence between \(E_0\) and the pore width, \(x\), is given by\textsuperscript{20,21,23,25,28}

\[E_0 = 2k/x\]  (4)

where \(k\) is an empirical constant that varies slightly with the nature of the adsorbent.\textsuperscript{21} In most cases, however, \(k\) has been found to be approximately equal to 120 kJ Å/mole, which is the value used in this work.

Eqs 3 and 4 have been extended for predicting the pore size distribution by assuming a PSD function, \(f(x)\), and then using it to obtain the overall adsorption isotherm according to

\[W = \int_0^∞ W f(x) \, dx\]  (5)

where \(W\) now represents the volume adsorbed in a pore of width \(x\). The most commonly used form of \(f(x)\) has been the Gaussian distribution defined in terms of pore width,\textsuperscript{20} which is written as

\[f(x) = \frac{1}{\delta \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{x - x_0}{\delta} \right)^2 \right]\]  (6)

where \(\delta\) and \(x_0\) are the dispersion term and mean pore width, respectively. Substituting eqs 3, 4, and 6 into eq 5 gives the Dubinin–Stoeckli (DS)\textsuperscript{20} adsorption isotherm as

\[W = \frac{W_0}{2\sqrt{1 + 2m\delta^2}} \exp \left[ -\frac{m\delta^2}{1 + 2m\delta^2} \right] 1 + \frac{x_0}{\delta \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{x_0}{\sqrt{2\delta}} \right)^2 \right]\]  (7)

where \(m = (1/2\beta k)^2\). This equation, and other forms of potential theory modified for heterogeneous adsorbents, has been reported to be reliable only for low relative pressures.\textsuperscript{18,23} Therefore, a new approach is taken in this study wherein a multisegment version of eq 7 is used to account for relative pressures \((P_r)\) in the overall range between zero and one.

This new approach requires that the overall range of \(P_r\) be divided into several segments and that the adsorption isotherm data in each segment be fitted independently according to eq 7. The resulting overlapping pore size distributions are then cut off at their points of intersection, which produces an essentially continuous PSD from the discrete PSDs. The total pore volume is then obtained by averaging according to

\[W_{\text{tot}} = \frac{1}{\sum_{j=\text{segment 1}}^J} \frac{p_j W_{\text{seg j}}}{\sum_{j=\text{segment 1}}^J p_j}\]  (8)

where \(J\) is the total number of relative pressure segments applied to the adsorption isotherm data; \(W_0\) is the fitted pore size volume, \(W_{\text{seg j}}\), for \(P_r\), segment \(j\); and \(p_j\) is a weighing factor that represents the relative significance of the pore volume utilized in segment \(j\) to the total pore volume. An expression for \(p_j\) was obtained empirically from the probability of occurrence of pore sizes in segment \(j\) relative to the overall PSD. This relative probability is estimated from

\[p_j = \frac{\int_{x_{j-1}}^{x_j} f(x) \, dx}{\int_0^∞ f(x) \, dx}\]  (9a)

where \(x_{j-1}\) and \(x_j\) are the lower and upper cutoff limits, respectively, for the PSD of \(P_r\) segment \(j\) with \(x_0 = 0\) and \(x_∞ = \infty\). \(NJ\) is the total number of pressure segments. \(f(x)\) is the PSD function of increment \(j\) and given by eq 6 in terms of the parameters \(x_0\) and \(\delta_j\), which are the fitted values of \(x_0\) and \(\delta\) for segment \(j\). Substituting eq 6 for segment \(j\) into eq 9a and simplifying leads to

\[p_j = \left[ \frac{\text{erf}(\frac{x_j - x_0}{\sqrt{2}\delta_j}) - \text{erf}(\frac{x_{j-1} - x_0}{\sqrt{2}\delta_j})}{1 + \text{erf}(\frac{x_0}{\sqrt{2}\delta_j})} \right]\]  (9b)

In contrast, the total pore volume predicted from the one-segment approach results in a total pore volume of \(W_{\text{tot}} = W_0\).

**Experimental Section**

**Materials.** CP-grade helium, methane, ethane, and n-pentane were obtained from National Welders. CP-grade propane was obtained from Matheson Gas Products, Inc. n-Pentane and n-heptane were >99% pure and were obtained from Alfa Aesar, and n-hexane was >99% pure and was obtained from Sigma Chemicals Company. All of these adsorbates were used as received. The BAX-1100 activated carbon was obtained from Westvaco in the form of pellets (2.1 mm extruded) and used as received, except for regeneration.

**Adsorption Equilibria Measurement and Adsorbent Characterization.** Adsorption equilibria for methane, ethane, propane, n-pentane, n-hexane and n-heptane on BAX-1100 activated carbon were measured gravimetrically using a VTI integrated microbalance system driven with in-house-developed National Instruments LabView hardware and software. Typically, 80–150 mg of activated carbon were loaded into the system, depending on the n-alkane being investigated. Prior to each isotherm measurement, the activated carbon was regenerated at 523 K for 2 h under a vacuum of less than 1 × 10⁻⁵ Torr. Precision was confirmed by carrying out multiple runs with different...
adsorbent samples and repeated runs with the same sample; virtually identical results were obtained in all cases. Accuracy was confirmed by reproducing an n-butane isotherm on BAX-1100 activated carbon at 298 K that was supplied by Westvaco; when plotted, the two isotherms were indistinguishable. Also, buoyancy cor-

Figure 1. Adsorption equilibria of the normal alkane series C_1–C_7 on BAX-1100 activated carbon. Symbols represent experimental data, and lines represent predictions from eq 12, the potential theory characteristic curve correlation (Figure 2). Asterisks denote isotherms measured but not plotted here for clarity.
Table 1. Ranges of Experimental Conditions for the Adsorption Equilibria of the n-Alkane Series C₁⁻C₇ on BAX-1100 Activated Carbon and Some Thermodynamic Parameters of the Adsorbates

<table>
<thead>
<tr>
<th>alkane</th>
<th>Nₐ</th>
<th>P (Torr)</th>
<th>T (K)</th>
<th>ϵ (cm³/mole)</th>
<th>T_nbp (K)</th>
<th>T_c (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>181</td>
<td>3.96⁻⁴.964</td>
<td>293⁻³.343</td>
<td>7.343</td>
<td>111.67</td>
<td>647.28</td>
</tr>
<tr>
<td>C₂</td>
<td>823</td>
<td>0.08⁻⁴.948</td>
<td>293⁻³.363</td>
<td>7.882</td>
<td>184.56</td>
<td>305.56</td>
</tr>
<tr>
<td>C₃</td>
<td>897</td>
<td>0.10⁻⁴.953</td>
<td>293⁻³.363</td>
<td>10.348</td>
<td>231.11</td>
<td>369.94</td>
</tr>
<tr>
<td>n-C₄</td>
<td>869</td>
<td>0.06⁻¹.494</td>
<td>293⁻³.363</td>
<td>12.994</td>
<td>272.67</td>
<td>425.17</td>
</tr>
<tr>
<td>n-C₅</td>
<td>812</td>
<td>0.07⁻¹.000</td>
<td>293⁻³.363</td>
<td>15.268</td>
<td>309.22</td>
<td>469.78</td>
</tr>
<tr>
<td>n-C₆</td>
<td>323</td>
<td>0.06⁻¹.000</td>
<td>293⁻³.363</td>
<td>17.638</td>
<td>341.89</td>
<td>507.89</td>
</tr>
<tr>
<td>n-C₇</td>
<td>373</td>
<td>0.15⁻.58</td>
<td>293⁻³.393</td>
<td>20.052</td>
<td>371.61</td>
<td>540.17</td>
</tr>
</tbody>
</table>

Results and Discussion

Potential Theory Correlation. The experimental adsorption equilibria of the C₁⁻C₇ n-alkane series on BAX-1100 activated carbon are summarized in Table 1. Temperatures ranged from 293 to 393 K, pressures ranged from 0.06 to 4964 Torr, and the number of data points ranged from 181 to 897, depending on the n-alkane. The complete set of tabulated data is available in an electronic (Microsoft Excel) format from the corresponding author or as Supporting Information.

Figure 2 displays the characteristic curve obtained by correlating all of the experimental adsorption equilibria with the potential theory model described by eqs 1 and 2. The coalescing factors, β, were optimized geometrically in reference to ethane, which was given the reference value of 1. The resulting values are listed in Figure 2. Notice that, in general, β decreased with increasing carbon number; however, no specific trend was observed that allowed β to be correlated with the carbon number. This characteristic curve was fitted to A using the least sum square error (LSSE) method in the logarithm of the total volume of the adsorbed phase, ln(nv), according to the following objective function:

\[ F' = \min \left( \sum_{N=1}^{N_P} \left[ \sum_{i=1}^{N} \left( \ln(\text{nv}^{\text{corr}}) - \ln(\text{nv}^{\text{exp}}) \right) \right] \right) \] (10)

This low value of the overall ARE indicates that eq 12 satisfactorily represents the whole system of adsorption equilibria; therefore, this potential theory correlation is quite accurate over a broad range of experimental conditions.
Predicted Pore Size Distributions. The pore size distribution obtained from the ASAP2010 via a DFT analysis is shown in Figure 3, along with the experimental nitrogen isotherm (symbols) and the corresponding fit to this isotherm with DFT (solid lines). The ASAP2010 provides a standard software package for estimating the PSD from the measured adsorption equilibria via a DFT method. This software has only one input parameter, the regularization parameter (RP), which can be set to one of four values: none, low, medium, and high. It is noteworthy that the low, medium, and high values all gave nearly identical results (not shown) in both the predicted adsorption isotherm and the resulting PSD, which added confidence to the convergence of the optimization method. The results in Figure 3 correspond to the medium value of RP, and they show that the DFT method was capable of reproducing the nitrogen isotherm extremely well, which lends credence to the PSD obtained in this manner. This PSD exhibits three distinct peaks at about 6, 12, and 25 Å, whereas a broad shoulder begins at about 40 Å and extends to about 300 Å, the upper limit of the applicability of the DFT method. Also, the smallest pores identified by nitrogen filling are about 4 Å, in agreement with the molecular diameter of nitrogen being about 3.7 Å, as estimated from the Lennard-Jones parameter (σ). Therefore, BAX-1100 activated carbon contains a fair amount of structural heterogeneity within a multinodal distribution of pore sizes and with a large fraction of the pore volume associated with mesopores. The total pore volume and BET surface area of the BAX-1100 activated carbon were also obtained from the ASAP2010 analysis as 0.799 cm³/g and 1251 m²/g, respectively. With the PSD predicted satisfactorily from DFT, and accepting the fact that this state-of-the-art technique produces the best possible estimate of the actual PSD of the BAX-1100 activated carbon, the DFT PSD was used to evaluate the creditability of the different alkane adsorption isotherms to provide an approximation of the PSD by applying the isotherms to different potential theory PSD prediction methods.

Three different potential theory approaches were examined for predicting the PSD of the BAX-1100 activated carbon from the experimental adsorption equilibria for each adsorbate in the n-alkane series C₁–C₇. The first two approaches adopted in this work were based on the popular, one-segment Gaussian distribution that leads to the DS potential theory equation. However, the DS and other similar models were reported to be reliable only in the low range of relative pressures for predicting the PSD. Therefore, to further examine this reliability, the one-segment approach was applied in this work with Pᵢ limits of both 0.3 and 1.0. The third approach corresponds to the multisegment Gaussian distribution approach discussed earlier. Note that, because the objective here was to evaluate each adsorbate independently from the other adsorbates, β was set to unity for each of the n-alkanes for all three potential theory approaches.

For the multisegment approach, five segments were found to be efficient for fitting the extensive experimental data set presented in this work. Thus, the experimental data were divided into five segments, numbered with roman numerals i through v, with Pᵢ ranges of (i) 0–0.005, (ii) 0.005–0.03, (iii) 0.03–0.1, (iv) 0.1–0.6, and (v) 0.6–1.0, whenever these ranges existed within the experimental data set. Values of A were recalculated with R = 8.314 J mol⁻¹ K⁻¹, and the adsorption equilibria in each segment were fitted independently to eq 7 by minimizing the following objective function for each of the n-alkanes:

$$ F = \min_\{W\} \sum_{i=1}^{N_j} \left( \ln W_{calc}^\{\text{exp} \} - \ln W_{calc}^\{\text{corr} \} \right)^2 $$  

where j is the Pᵢ segment number, N_j is the number of experimental data points within segment j, W_{calc}^\{\text{exp} \} = n_{calc}^\{\text{exp} \} × v, n_{calc}^\{\text{exp} \} is the experimental amount adsorbed, and W_{calc}^\{\text{corr} \} is the correlated adsorbed-phase volume estimated from eq 7. The corresponding ARE values, estimated from eq 15 (with N_j instead of N), and the optimum fitting parameters are shown in Table 2.

$$ \text{ARE}(\%) = \frac{100}{N_{p_j}} \sum_{i=1}^{N_{p_j}} \left| \frac{n_{exp}^i - n_{corr}^i}{n_{exp}^i} \right| $$  

The pore volume distribution in terms of pore sizes is given by Wₙ(x), where W₀ is the fitted total pore volume and f(x) is calculated from eq 6 with the fitted values of x₀ and β. Similar analyses were carried out for the two one-segment approaches but with Pᵢ ranges fixed from 0–0.3 and 0–1.0; thus, j = 1 in both cases, and only the ARE values are reported in Table 2. It was not surprising that the ARE values were, in general, much higher for the one-segment approaches compared to the multisegment approach. The PSDs obtained from the multiseg-
Table 2. DS Potential Theory Correlation Parameters and Corresponding ARE Values Obtained from Fitting the Adsorption Equilibria of the n-Alkane Series C1–C7 on BAX-1100 Activated Carbon to the New Multisegment and the Original One-Segment Gaussian Pore Size Distribution Models

<table>
<thead>
<tr>
<th>P&lt;sub&gt;r&lt;/sub&gt; segment</th>
<th>parameter</th>
<th>C&lt;sub&gt;1&lt;/sub&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;</th>
<th>C&lt;sub&gt;3&lt;/sub&gt;</th>
<th>C&lt;sub&gt;4&lt;/sub&gt;</th>
<th>C&lt;sub&gt;5&lt;/sub&gt;</th>
<th>C&lt;sub&gt;6&lt;/sub&gt;</th>
<th>C&lt;sub&gt;7&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>W&lt;sub&gt;0&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/kg)</td>
<td>297.6</td>
<td>296.3</td>
<td>330.7</td>
<td>426.2</td>
<td>480.4</td>
<td>522.3</td>
<td>590.2</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;0&lt;/sub&gt; (Å)</td>
<td>27.166</td>
<td>24.122</td>
<td>19.557</td>
<td>17.860</td>
<td>15.663</td>
<td>14.555</td>
<td>13.454</td>
</tr>
<tr>
<td>0 &lt; P&lt;sub&gt;r&lt;/sub&gt; &lt; 0.005</td>
<td>δ (Å)</td>
<td>4.115</td>
<td>4.577</td>
<td>2.789</td>
<td>3.232</td>
<td>2.414</td>
<td>3.414</td>
<td>3.311</td>
</tr>
<tr>
<td></td>
<td>ARE (%)</td>
<td>14.55</td>
<td>8.53</td>
<td>4.61</td>
<td>1.81</td>
<td>3.08</td>
<td>2.61</td>
<td>3.76</td>
</tr>
<tr>
<td>ii</td>
<td>W&lt;sub&gt;0&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/kg)</td>
<td>378.4</td>
<td>472.2</td>
<td>496.7</td>
<td>532.4</td>
<td>584.5</td>
<td>621.7</td>
<td>779.8</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;0&lt;/sub&gt; (Å)</td>
<td>30.102</td>
<td>29.518</td>
<td>23.657</td>
<td>20.189</td>
<td>18.197</td>
<td>16.526</td>
<td>16.783</td>
</tr>
<tr>
<td>0.005 &lt; P&lt;sub&gt;r&lt;/sub&gt; &lt; 0.03</td>
<td>δ (Å)</td>
<td>7.718</td>
<td>9.221</td>
<td>6.164</td>
<td>5.839</td>
<td>6.527</td>
<td>7.709</td>
<td>9.757</td>
</tr>
<tr>
<td></td>
<td>ARE (%)</td>
<td>4.02</td>
<td>5.71</td>
<td>2.20</td>
<td>2.58</td>
<td>1.98</td>
<td>2.16</td>
<td>4.24</td>
</tr>
<tr>
<td>iii</td>
<td>W&lt;sub&gt;0&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/kg)</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>561.8</td>
<td>590.1</td>
<td>1507.3</td>
<td>905.6</td>
<td>1534.8</td>
<td>943.7</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;0&lt;/sub&gt; (Å)</td>
<td>32.936</td>
<td>26.616</td>
<td>0.000</td>
<td>16.993</td>
<td>0.000</td>
<td>15.056</td>
<td></td>
</tr>
<tr>
<td>0.03 &lt; P&lt;sub&gt;r&lt;/sub&gt; &lt; 0.10</td>
<td>δ (Å)</td>
<td>17.585</td>
<td>14.183</td>
<td>40.820</td>
<td>20.727</td>
<td>30.502</td>
<td>16.387</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ARE (%)</td>
<td>1.76</td>
<td>0.91</td>
<td>1.98</td>
<td>0.98</td>
<td>1.56</td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td>iv</td>
<td>W&lt;sub&gt;0&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/kg)</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>30.912</td>
<td>1285.4</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a,b</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;0&lt;/sub&gt; (Å)</td>
<td>15.577</td>
<td>44.841</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10 &lt; P&lt;sub&gt;r&lt;/sub&gt; &lt; 0.60</td>
<td>δ (Å)</td>
<td>0.50</td>
<td>2.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v</td>
<td>W&lt;sub&gt;0&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/kg)</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1502.4</td>
<td>1586.2</td>
<td>NA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2228.7</td>
<td>1770.3</td>
</tr>
<tr>
<td></td>
<td>x&lt;sub&gt;0&lt;/sub&gt; (Å)</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>84.106</td>
<td>32.472</td>
<td>146.494</td>
<td>44.365</td>
<td></td>
</tr>
<tr>
<td>0.60 &lt; P&lt;sub&gt;r&lt;/sub&gt; &lt; 1.00</td>
<td>δ (Å)</td>
<td>1.90</td>
<td>2.03</td>
<td></td>
<td></td>
<td>0.00</td>
<td>2.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ARE (%)</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>146.949</td>
<td>44.365</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>one-segment</td>
<td>W&lt;sub&gt;0&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/kg)</td>
<td>574.8</td>
<td>408.3</td>
<td>459.4</td>
<td>597.5</td>
<td>601.9</td>
<td>686.9</td>
<td>684.6</td>
</tr>
<tr>
<td>0.0 &lt; P&lt;sub&gt;r&lt;/sub&gt; &lt; 0.30</td>
<td>δ (Å)</td>
<td>4.522</td>
<td>5.094</td>
<td>3.860</td>
<td>4.767</td>
<td>4.121</td>
<td>8.432</td>
<td>6.060</td>
</tr>
<tr>
<td></td>
<td>ARE (%)</td>
<td>15.44</td>
<td>7.83</td>
<td>5.43</td>
<td>5.19</td>
<td>3.75</td>
<td>2.86</td>
<td>4.82</td>
</tr>
<tr>
<td>one-segment</td>
<td>W&lt;sub&gt;0&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;/kg)</td>
<td>same</td>
<td>same</td>
<td>496.1</td>
<td>639.7</td>
<td>same</td>
<td>750.6</td>
<td>743.7</td>
</tr>
<tr>
<td>0.0 &lt; P&lt;sub&gt;r&lt;/sub&gt; &lt; 1.00</td>
<td>δ (Å)</td>
<td>(max P&lt;sub&gt;r&lt;/sub&gt; &lt; 0.3)</td>
<td>22.316</td>
<td>21.289</td>
<td>max P&lt;sub&gt;r&lt;/sub&gt; &lt; 0.3</td>
<td>19.069</td>
<td>16.918</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ARE (%)</td>
<td>(max P&lt;sub&gt;r&lt;/sub&gt; &lt; 0.3)</td>
<td>4.156</td>
<td>5.256</td>
<td>4.156</td>
<td>5.256</td>
<td>4.156</td>
<td>5.256</td>
</tr>
</tbody>
</table>

<sup>a</sup> Heavy alkanes exhibit the same behavior in segments iii and iv; thus, segment iii is extended to also cover segment iv. <sup>b</sup> Segment v for n-heptane starts at P<sub>r</sub> = 0.5 instead of 0.6. <sup>c</sup> NA = No available experimental data in the corresponding segment.

mation approach (thin solid lines) and from the one-segment approaches are displayed in Figure 4 (dashed and dash-dotted lines) for each of the n-alkanes. For comparison, the PSD obtained from DFT is also displayed in each of the panels in Figure 4 (thick solid lines).

In all cases, the one-segment models predicted nearly identical trends, independent of the P<sub>r</sub> range. For example, the smaller alkanes were qualitatively more descriptive of the PSD in the mesopore region, the widths of the PSDs increased with increasing carbon number in the n-alkane series, and the average pore sizes decreased with increasing carbon number in the n-alkane series from about 30 Å to about 15 Å. Moreover, as the widths increased, the one-segment Gaussian distributions began to capture more of the multinodal PSD obtained from DFT; however, up to n-pentane, pores less than 10 Å in diameter and greater than 30 Å in diameter were not predicted. For n-hexane and n-heptane, the widths of the PSDs increased so much that they severely overpredicted the distribution of pores less than 10 Å but still did not capture those greater than 35 Å. In contrast, the multisegment approach produced more skewed but essentially continuous distributions (thin solid lines) by truncating each distribution at the meeting point with the subsequent segment. Like the one-segment models, these multisegment distributions widened and shifted to smaller pores with increasing carbon number in the n-alkane series. Again, up to n-pentane, pores less than 10 Å were not predicted. However, the multisegment model increasingly captured more of the mesopore size distributions, and for n-hexane and n-heptane, the PSDS agreed at least qualitatively with that obtained from DFT, capturing both the smaller micropores and some of the larger mesopores.

Another alternative approach was to truncate only the f(x) curves (without multiplying them in each segment by the corresponding W<sub>0</sub> value). This resulted in the continuous pore size distributions shown in Figure 5. The resulting cutoff pore sizes from these two multisegment approaches deviated only slightly from each other, as shown in Table 3. The total (cumulative) pore volumes were calculated from eq 8 with the segment number replacing J. Table 3 shows the relative errors in these total pore volumes predicted from both multisegment approaches and the corresponding truncation limits of P<sub>r</sub>. Table 3 also gives the relative errors in the total pore volumes predicted from the W<sub>0</sub> values obtained from the one-segment approaches with the experimental adsorption isotherms truncated at P<sub>r</sub> = 0.3 and P<sub>r</sub> = 1.0. Clearly, the adsorption equilibria of the larger n-alkanes fitted with any of the different potential theory models provided more accurate predictions of the total pore volume. However, a significant improvement in the accuracy was obtained when the multisegment approach was used with the adsorption equilibria truncated at the proper pressure limits. Also, the predictions with the cutoff pore sizes determined from the continuity of the pore size distributions, f(x), were more accurate than those determined with the cutoff pore sizes determined from the continuity of the adsorbed-phase volume distributions, W<sub>0</sub> × f(x). Moreover, although the predicted pore volumes from the smaller alkane molecules were acceptably close to the experimental values, no reliable limit of relative pressures was clearly observed for pore filling. In other words, it appeared that C<sub>1</sub> and C<sub>2</sub> did not condense and...
thus did not fill the total pore volume over the pressure ranges studied. This was not the case, however, for the heavier alkanes. Propane clearly exhibited a pore-filling relative pressure within the $P_r$ range investigated, as evidenced by the total volume being within 2% of the experimental value. Moreover, a simple investigation of the pore-filling relative pressures for components heavier than C3, for which sufficient data were available, revealed that the total pore volume was most accurately predicted at relative pressures of 1, 0.6, and 0.5 for C4, C6, and C7, respectively. Experimental data for C5 were measured only up to a maximum relative pressure of approximately 0.24. Therefore, although the latter investigation could not be conducted on the C5 adsorption isotherms, it is expected that the most accurate prediction of the total pore volume with the proposed method would be exhibited at a relative pressure between 0.6 and 1. These relative pressure limits were understood to correspond roughly to the pore-filling or condensation limits of these adsorbates. The error in predicting the total pore volume under these conditions was, in most cases, around or below 1% of the experimental value, as shown in Table 3.

Overall, these results suggest that the potential theory methods should be used with caution for predicting the PSD of an adsorbent. For example, the results

![Figure 4](image1.png)  
**Figure 4.** Comparison of pore volume distributions of the BAX-1100 activated carbon obtained from DFT (thick solid line) and predicted from the new multisegment model (thin solid line) and the two original one-segment models with upper $P_r$ limits of 0.3 (dashed lines) and 1.0 (dash-dot lines) for each of the n-alkanes.

![Figure 5](image2.png)  
**Figure 5.** Pore size distributions predicted from the new multisegment model for each of the n-alkanes adsorbed on BAX-1100 activated carbon.
A very extensive set of single-component adsorption equilibria for the n-alkane series C1–C7 on Westvaco BAX-1100 activated carbon was measured over very broad ranges of temperature and pressure. A potential theory model correlated well with all of the data, and the predictions were better than those obtained on the basis of a one-segment Gaussian distribution approach suggested in the literature. In fact, the results from the new approach can be used to more accurately examine the pore-filling pressure ranges of the n-alkanes C3–C7 because this new multisegment approach resulted in a skewed pore size distribution for the heavier n-alkanes that actually mimicked the monodisperse pore size distribution from density functional theory. It is not possible to obtain a skewed pore size distribution from the one-segment Gaussian approach. This extensive data set should also be useful for testing other adsorbent characterization schemes based on potential theory and other models.

Finally, this data set should prove to be very useful for predicting the behavior of hydrocarbon separation and purification processes, using BAX-1100 activated carbon as the adsorbent. It should prove to be especially useful for predicting the nonisothermal behavior of these processes, because the adsorption process models can be applied over very broad ranges of temperature and pressure (and thus loading) without resorting to extensive extrapolation of the data. The isosteric heats of adsorption and adsorbed-phase heat capacities that can be used in modeling the nonisothermal behavior of these systems are evaluated in Part 2 of this series.

**Acknowledgment**

The authors gratefully acknowledge financial support from the National Science Foundation under Grant CTS-9503632, the Westvaco Charleston Research Center, and the Separations Research Program at the University of Texas at Austin.

**Supporting Information Available:** Complete set of tabulated data for the experimental adsorption equilibria of the C1–C7 n-alkane series on BAX-1100 activated carbon. This material is available free of charge via the Internet at http://pubs.acs.org.

**Literature Cited**


### Table 3. Truncation Limitsa for the Multisegment Gaussian Pore Size Distributions and Average Relative Errorsb in the Corresponding Total Pore Volumes Predicted from the Adsorption Equilibria of the n-Alkane Series C1–C7 on BAX-1100 Activated Carbon

<table>
<thead>
<tr>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
</tr>
</thead>
<tbody>
<tr>
<td>x_{W} (Å)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>x_{W} (Å)</td>
<td>21.25</td>
<td>17.20</td>
<td>14.85</td>
<td>13.00</td>
<td>11.80</td>
<td>9.62</td>
</tr>
<tr>
<td>x_{W} (Å)</td>
<td>∞</td>
<td>39.00</td>
<td>31.00</td>
<td>29.00</td>
<td>26.60</td>
<td>26.55</td>
</tr>
<tr>
<td>x_{W} (Å)</td>
<td>90.00</td>
<td>45.40</td>
<td>40.00</td>
<td>∞</td>
<td>47.70</td>
<td>33.80</td>
</tr>
<tr>
<td>x_{W} (Å)</td>
<td>∞</td>
<td>52.20</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>d</td>
</tr>
<tr>
<td>x_{W} (Å)</td>
<td>∞</td>
<td>∞</td>
<td>NA</td>
<td>∞</td>
<td>∞</td>
<td></td>
</tr>
</tbody>
</table>

a x_{W} and x_{R} are the lower and upper cutoff pore size limits from the pore volume distribution curves, and x_{D} and x_{A} are the corresponding limits from the f(x) curves. b W_{exp} and W_{cal} are the measured and predicted total pore volumes, respectively. Predicted values are obtained from eq 8 with J equal to the corresponding segment number and the appropriate cutoff limits (on either the W or the f basis, see the previous point). c Heavy alkanes exhibit the same behavior in segments iii and iv; thus, segment iii is extended to also cover segment iv. d Segment v for n-heptane starts at P_{f} = 0.5 instead of 0.6. e g_{L_1} and g_{L_1} are the relative errors (defined as in note b) in predicting the total pore volumes from the one-segment Gaussian pore size distributions and experimental isotherms truncated at P_{f} = 0.5 and 1.0, respectively. f NA = No available experimental data in the corresponding segment.


Received for review May 10, 2000
Accepted September 6, 2000