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Generalized High Pressure Gas Adsorption Model

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Abstrak

Pengetahuan mengenai perilaku adsorpsi terutama pada tekanan tinggi merupakan hal yang penting dalam proses yang melibatkan adsorpsi tekanan tinggi seperti pemisahan gas, penyimpanan gas, dan pengurangan emisi CO_2. Namun, penelitian tentang adsorpsi tekanan tinggi boleh dikatakan sangat jarang, juga model yang dapat secara akurat merepresentasikan adsorpsi tekanan tinggi. Model yang akurat serta mempunyai dasar teori yang kuat dapat memperbaiki kemampuan model dalam memperkirakan adsorpsi gas, jika data eksperimen tidak ada. Dengan demikian, pengembangan model baru dibutuhkan untuk mengatasi beberpa kekurangan pada model yang ada. Di dalam studi ini, model-model adsorpsi berdasarkan teori teori Lattice Ono-Kondo (OK), dievaluasi dan dikembangkan lebih jauh untuk memperbaiki kemampuan prediksinya dalam menangani sistem adsorpsi pada kondisi dekat-kritis dan super-kritis. Tujuan dari pengembangan ini adalah untuk menghasilkan metoda penghitungan yang dapat diandalkan dan untuk meningkatkan pemahaman terhadap fenomena yang ada. Kemampuan dari model OK dengan dua parameter ditunjukkan oleh kemampuannya dalam merepresentasikan data adsorpsi dengan rata-rata 3.6% deviasi. Model OK yang digeneralisasikan juga dapat memprediksi adsorpsi gas pada karbon aktif dengan deviasi sebesar 8%. Lebih jauh lagi model ini juga mempunya potensi untuk memperkirakan adsorpsi gas lain didasarkan dari data adsorpsi isothermal satu gas dengan cukup akura.

Kata kunci: *Model adsorpsi, adsorpsi gas, tekanan tinggi dan karbon aktif*

Abstract

Knowledge of the adsorption behavior especially at high pressure, has been long been important in processes involving high pressure gas adsorption such as: gas separation, gas storage, and CO_2 sequestration. However, research on high pressure adsorption is considerably rare, also model that can accurately represent high pressure gas adsorption. Accurate model which has a strong theoreticl base can improve model ability to predict gas adsorption when experimental data are not available. Therefore, the new model need to be developed to overcome the discrepancies of the existing model. In this study, we evaluate and further develop adsorption models based the Ono-Kondo (OK) theory to improve their predictive capabilities when dealing with near-critical and supercritical adsorption systems. The goal of such developments is to facilitate the use of reliable computational frameworks for representing adsorption behavior, as well as improving our understanding of the phenomenon. The abilities of the two-parameter OK models to correlate accurately supercritical adsorption systems are demonstrated by representing the adsorption data with 3.6% AAD on average. The generalized OK model can also predict the adsorption on activated carbon with 8% AAD. Furthermore, a high potential exist the model that provides reasonably accurate predictions for other gases adsorption isotherms based on adsorption data for one gas at given temperature.

Keywords: *Adsorption model, gas adsorption, high-pressure and activated carbon*

1. Introduction

Understanding of gas adsorption, especially at high pressure, has been long been important in the application involving high pressure gas adsorption such as: gas separation, gas storage (Compressed Natural Gas, Hydrogen Storage dll), methane production and CO_2 sequestration in Coalbed Methane, etc. However, research on high pressure adsorption is considerably rare, also model that can

accurately represent high pressure gas adsorption.

The theory widely used for modeling adsorption such as the Langmuir model is not suitable anymore for high pressure adsorption. This limitted application of the Langmuir model is mainly due to: no correction on the adsorbed phase density which is very important at high pressure, assumtion of monolayer, no distinct correlation on tempereature dependence, no description on the physical properties of the adsorbate and adsorbent characteristics, and inappropriately applied for mixed gas adsorption. Meanwhile, understanding of how the adsorbed molecules interact with the other molecules and adsorbent molecules is important, not only to generate more accurate model but also to construct a strong theoreticl base in order to improve model ability to predict gas adsorption when experimental data are not available. Therefore, the new model need to be developed to overcome the discrepancies of the existing model.

The characteristic of the new model should fullfil the following criteria:

1. Able to take into account of the effect of adsorbed phase density at high pressure (up to 20 atm).
2. Able to represent experimental data with the accuracy within the uncertainties of the experimental data.
3. Able to correlate adsorption capacity with gas physical properties and adsorbent characteristics.
4. Able to predict gas adsorption at different temperature if gas adsorption data at given isothermal is available.
5. Able to predict different gas adsorption if certain isothermal gas adsorption on certain adsorbent is available.
6. Able to show good prediction ability (less than 10 % deviation).
7. Easy to be developed further for mixed gas adsorption prediction.

2. Ono-Kondo Adsorption Model

One of the model having potential to be developed further according to the abovementioned criteria is the lattice model firstly developed by Ono-Kondo [1]. This model was used by Donohue, et.al. [2] for modeling of component adsorption in a solution and seems suitable to be developed further for high pressure gas adsorption. Despite its strong theoretical base, the model also offers several practical advantages

In the OK model, fluid system is assumed consist of latice cells occupied by fluid molecules or just empty cells. When the adsorption occurs (Figure 1), more molecules will occupy cells in the adsorbed phase layer than in the gas phase (bulk).

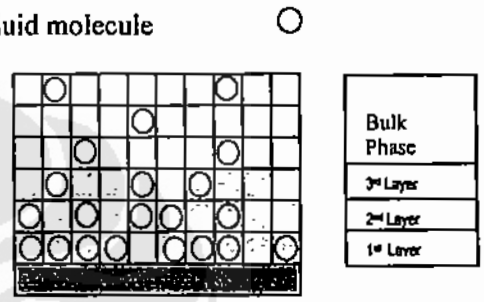

Figure 1.
Multi-Layer Adsorption

Molecular interactions occur between neighborhood molecules. At equilibrium, the free energy configuration of the first layer and the above layers results in the following gas adsorption equilibrium equation for layer t = 2,3, ...m (number of layers):

$$ln\left[x_t(1-x_b)/x_b(1-x_t)\right]+z_0(x_t-x_b)\varepsilon_{ss}/kT+(x_{t-1}-2x_t+x_{t+1})\varepsilon_{ss}/kT=0 \quad (1)$$

And gas adsorption equilibrium for the first layer:

$$ln\left[x_1(1-x_b)/x_b(1-x_1)\right]+(z_1x_1+x_2-z_0x_b)\varepsilon_{sf}/kT+\varepsilon_{ss}/kT=0 \quad (2)$$

While the total Gibbs adsorption is calculated using the following equation:

$$n_i^{Gibbs}=C_i\sum_{t=1}^{m}(x_{i,t}-x_{i,b}) \quad (3)$$

In the above equations, x_i is reduced density representing fraction of cells occupied by adsorbed molecule i at layer t

($= N_{i,t}/M_t$) and $z_1 = 6$, $z_0 = 8$ for hexagonal configuration, are numbers representing neighborhood molecules arrangement filling the cells. The fraction of occupied cells can also be presented as $x_{i,t} = \rho_{i,t} / \rho_{i,mc}$ and $x_{i,b} = \rho_{i,b} / \rho_{i,mc}$, where $\rho_{i,t}$ is the density of adsorbed component i at layer t, $\rho_{i,b}$ is the density of component i at gas phase, and $\rho_{i,mc}$ is the density of adsorbed component i at its maximum capacity. Parameter showing the energy interaction between adsorbate molecules is represented by ε_{ii}, and energy interaction parameter between adsorbate and adsorbent is written as ε_{is}. T is temperature absolute and k is Boltzman constant.

At Equation (3), parameter C represents maximum capacity of the adsorbent and can be considered as parameter related to number of active pores or other structural properties of the adsorbent. Number of layers, m, however, is specific for adsorbate-adsorbent system and need to be defined before using the model. This usually can be done by selecting appropriate number which give the best fit for experimental adsorption data.

Generalized formulation is important to predict other adsorption system, if experimental data are not available. Furthermore, since the model parameters are usually obtained from isothermal adsorption measurement, the temperature dependency of those parameters also need to be evaluated. The focus of this study is to propose correlation in generalized formulation for OK model parameters.

2. Research Method

In this study, the number of adsorption layers is determined by applying the model for several systems. Suitable number of layer will then be used for further study. In order to reduce the number of parameters in the model, two parameters of the model, i.e.: maximum adsorbed phase density and adsorbate-adsorbate energy interaction parameters are generalized based on the representation results of the model on selected systems. Two other parameters: C and ε_{is} are evaluated and further generalized.

In general, the new generalized model is evaluated through internal and external consistency test. Internal consistency of the model can be shown as ability of the model to represent experimental adsorption data with the accuracy within uncertainties of the experimental data. Model parameters are evaluated and further generalized using a regression method. About 3000 data points are used in this study. However, some data are not included in the model development step, but they are used to test the ability of the model to predict an isotherm adsorption system based on the generalized parameters obtained in the model development stage.

3. Results and Discussion

3.1. *Determination of the Number of Layers*

Table 1 shows the results of using monolayer and three-layer OK model to represent gas adsorption data of nitrogen, methane and CO_2 on an activated carbon at 45 °C, and adsorption data of CO_2 on a coal. Coal is selected to represent an adsorbent with a wide pore-size distribution. In this case, three parameters are fixed, and four other parameters are regressed to obtain minimum deviation from the eperimental data. Both models show excellent representation with 0,3 – 3,4 % AAD (Average Absolute Deviation), as such, comparable representation is observed for the monolayer and multilayer models.

The results suggest that the simpler monolayer model is appropriate for the systems considered. The results are not surprising, considering that the adsorption of small molecules occurs mostly in the micropore structure [3],[4]. Perhaps because the size of the micropores is only several times the diameter of the molecules and the phase conditions are removed from the critical region, monolayer adsorption is adequate.

Table 1.
Comparison of Different Layer Adsorption Model

Model Parameter	Activated Carbon			Coal
	N2	CH4	CO_2	CO_2
1-Layer				
ε_{ii}/k (K)	-1032	-1385	-1690	-1170
ε_{ij}/k (K)	41	64	82	60
ρ_{mc} (g/cc)	0.67	0.34	0.98	0.95
C (mmol/g)	2.72	3.26	4.53	1.19
NPTS	22	18	52	11
% AAD	**0.3**	**0.6**	**2.8**	**2.9**
3 Layers				
ε_{ii}/k (K)	-1020	-1380	-1650	-1160
ε_{ij}/k (K)	50	64	82	70
ρ_{mc} (g/cc)	0.67	0.40	1.02	0.98
C (mmol/g)	2.81	3.20	4.58	1.23
NPTS	22	18	52	11
% AAD	**0.3**	**0.6**	**3.4**	**3.0**

3.2. *The Maximum Adsorbed Phase Density*

The OK model has four parameters: ρ_{mc}, ε_{ii}/k, ε_{ij}/k and C. To reduce the number of regressed parameters in the model, the maximum adsorbed-phase density, ρ_{mc}, is estimated independently. A commonly used approximation is the liquid density at the normal boiling point, as was done by Arri and Yee [5]. However, examination of the results from the OK model reveals that the adsorbed-phase densities generated by the OK model, as presented in Table 1, are less than the boiling point estimates and are closer to the reciprocal van der Waals co-volume estimates. Moreover, these values are also close to the "graphical estimates" based on the Gibbs adsorption definition (Equation 3). As shown in the figure for CO_2, if the absolute adsorption becomes constant at high pressures, then the Gibbs adsorption should show a linear decrease with increasing ρ_{gas}. Extrapolation of this linear relation yields an x-axis intercept where $\rho_{ads} = \rho_{gas} = \rho_{mc}$. Use of this technique requires sufficient data in the linear (high pressure) region beyond the maximum in the Gibbs adsorption; thus, an estimate is shown in Fig 2 only for carbon dioxide. For the other adsorbates, the available data do not extend into the linear region.

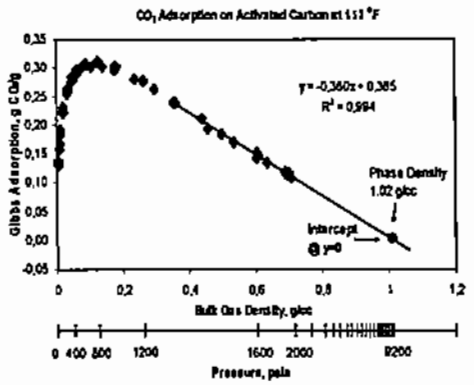

Figure 2.
Adsorbed Phase Density Estimate

3.3. The Fluid-fluid Energy Parameter

In the present work, the fluid-fluid energy parameter, ε_{ii}/k, was estimated to be proportional to the Lennard-Jones well depth energy parameter. Theoretically, the correlation can be derived resulting in the following estimate for the fluid-fluid energy parameter in the OK model:

$$\varepsilon_{ii} = 0.432\varepsilon^* \qquad (4)$$

The fluid-fluid energy parameters obtained for the gas adsorptions on activated carbon shown in Table 1 are reasonably close to the ones obtained from the above expression; for example, the regressed value of ε_{ii}/k for CO_2 is 82 K compared to the 84.3 K value estimated using Equation (4). Further, the value of the calculated Gibbs excess adsorption is not highly sensitive to small deviations in ε_{ii}/k obtained from Equation (4); for example, a ten percent deviation in ε_{ii}/k can still produce reasonable values of the Gibbs excess adsorption. We also observed that the fluid-fluid energy parameters are positive values, which represents a repulsive energy potential. These results confirm the observations of Benard and Chahine [4] and also agree with molecular simulation results obtained recently by Aranovich [6].

3.4. *Two-Parameter OK Model*

The adsorbed-phase density and the fluid-fluid energy parameters can be estimated from the reciprocal van der

Waals co-volume and from a proportional relation to the well depth of the Lennard-Jones 12-6 potential, respectively. For further generalization, the above estimates were applied for modeling of selected gas adsorption on activated carbon and zeolites reported in the literature. In this case, the fluid-solid energy parameter, ε_s/k, was regressed for each *system* and the parameter C was regressed for each adsorption *isotherm*. Because no detailed information was given on uncertainties in the selected literature experimental data, the percentage average deviation of the Gibbs excess adsorption (% AAD) was used as the objective function to determine the two model parameters.

Figure 3 shows the percentage deviation plot for the OK model representation of the adsorption data on activated carbon (2242 data points). About 90% of the data can be represented by the model within 8.4 % AAD, where the average is 3.6%. The large percentage deviations occurred mainly when the Gibbs excess adsorption values are small at relatively low pressures. Figure 4 illustrates the OK model representation of System 15 (CO_2 on Norit R1 Extra activated carbon), where the percentage deviations are large (9.5 % AAD). As shown in the figure, the model can actually represent the experimental data reasonably well at pressure above 0.5 MPa. The nitrogen and methane adsorption on the same activated carbon are also shown in the figure for comparison.

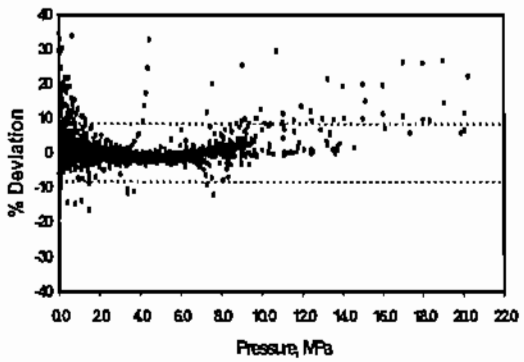

Figure 3.
Deviation Plot for Two-Parameter OK Model Representations of Gas Adsorption on Activated Carbon

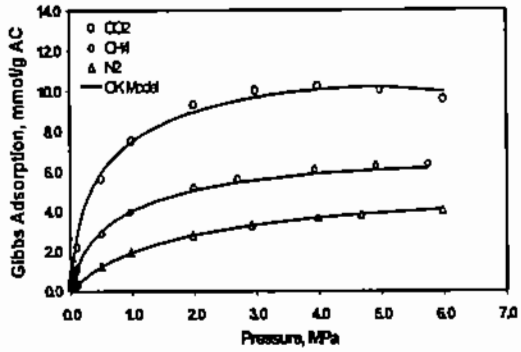

Figure 4.
OK Model Representations of Gas Adsorption on Norit R1 Extra Activated Carbon at 298 K [Data:7]

Figure 5 illustrates the OK model representation of a system with significant temperature range. As shown in this figure, the model is capable of describing the temperature variation.

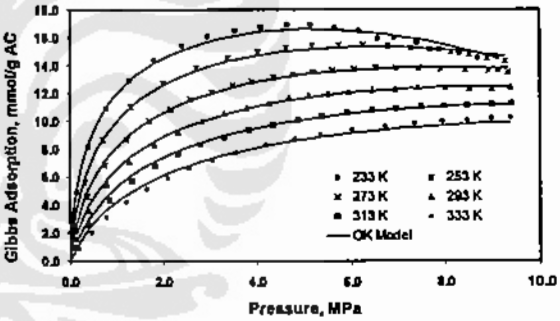

Figure 5.
K Model Representations of Methane Adsorption on Activated Carbon [Data: 8]

3.5. *Basis for Parameter Generalization*

Based on our preliminary evaluation of the regressed parameter C, it appears that, for a given adsorbate at fixed temperature, the value of C increases as the surface area of the adsorbent increases. Figure 6 presents the plots of parameter C obtained against the surface area, A. The values of the surface areas, in most cases, were reported by the investigators. In a few cases, however, they were obtained from the information provided by the adsorption production company or estimated from the literature. Although the accuracy of the reported surface areas is questionable,

Figure 6 still shows a reasonable linear correlation between the parameter C and the surface area, A.

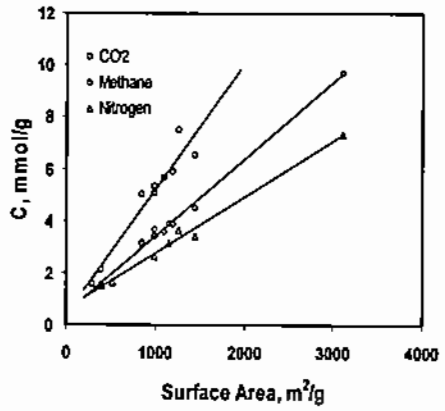

Figure 6.
Correlation of the Maximum Adsorption Capacity, C, with Surface Area at Constant Temperature

This suggests that the maximum adsorption capacity, C, can be divided into two contributions; i.e. the contribution from the adsorbent characteristic, represented by surface area (A, m^2/g), and the contribution from the adsorbate characteristic(s). In this study, we proposed the following simple relation for the maximum adsorption capacity, C:

$$C(T) = \frac{AC_a(T)}{2} \qquad (5)$$

C_a is the surface adsorbed-phase density ($mmol/m^2$), with its value depending only on the adsorbate.

C is also temperature dependent. As indicated in the regression results, value of C increases as temperature decreases. This temperature dependence of the maximum adsorption capacity is not uncommon, based on the previous studies. Benard and Chahine [4,9] reported the temperature dependence of C, and they proposed an empirical temperature relation for C. Similarly, Do [10] asserted that the maximum adsorption capacity in the Langmuir model was a function of temperature. He described this temperature dependence as due to the thermal expansion of the adsorbed phase. In our study, we propose the following correlation:

$$ln(1/C) = \delta T - [lnC_{a,o} + \delta T_o + ln(A/2)] \qquad (6)$$

where T_o (k) is chosen at the normal boiling point of the adsorbate (triple point for CO_2), T(K) is the absolute temperature, $C_{a,o}$ is the maximum surface adsorbed-phase density at T_o, and δ is the thermal expansion coefficient of the adsorbed phase.

For a given system, Equation (6) yields a linear correlation if $ln(1/C)$ is plotted against temperature, T. Figure 7 presents the correlation between $ln(1/C)$ obtained from Table 8 for gas adsorption on BPL activated carbon [11] and temperature, T. The linear relationship shown in this figure suggests that Equation (6) provides a good representation of the temperature dependence of the maximum adsorption capacity, C

The fluid-solid energy parameter, ε_{is}/k, was generalized based on the interaction of a single molecule with a single lattice plane. In this study we propose the following equation:

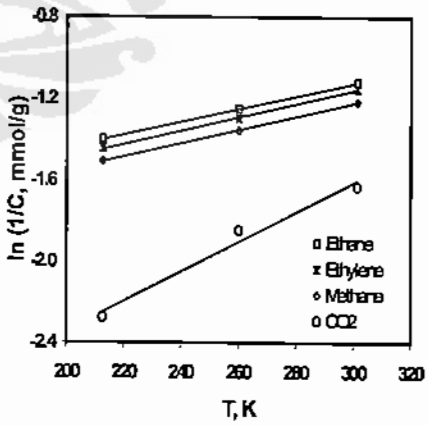

Figure 7.
Temperature Dependence Of The Maximum Adsorption Capacity, C, (Data: 11)

$$\varepsilon_{is} = -\frac{6}{5}\pi\rho_c\varepsilon^*_{iC}\sigma^2_{iC} \qquad (7)$$

where $\rho_c = 0.382$ atom/Å^2 is the area density of carbon atoms in a graphite plane. the adsorbate-carbon collision diameter is

estimated as $\sigma_{iC} = \frac{1}{2}(\sigma_{ii} + \sigma_{CC})$. The adsorbate-carbon well depth potential is estimated as $\varepsilon^{\bullet}_{iC} = \sqrt{\varepsilon^{\bullet}_{ii}\varepsilon^{\bullet}_{CC}}$.

Generalization of the model parameters was performed by evaluating $C_{a,o}$, δ and $\varepsilon^{\bullet}_{CC}$ of the systems studied. Figure 8 shows the deviation plot for OK generalized model of gas adsorption on activated carbon. The overall percentage deviations is about 8%. In this case, surface area used is based on reported surface area. For CO_2: $C_{a,o}$ = 0.0142 mmol/m^2; δ = 0.0039 (K^{-1}) and for other adsorbate: $C_{a,o} = 0.102/\sigma^2 + 0.0034$; σ in Å, and δ = 0.0024 (K^{-1}). ε_{cc}/k (K) is varied from 38 to 43.

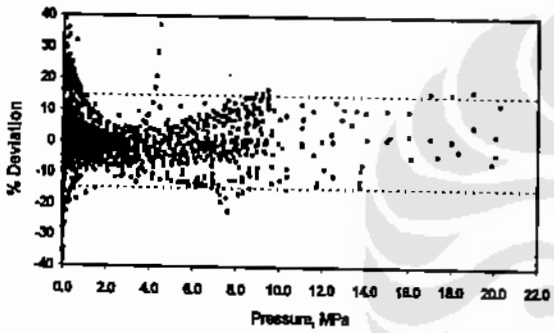

Figure 8.

Deviation Plot for the Generalized OK Model Predictions

Figure 9 illustrates the comparison of generalized and two-parameter OK model representation of methane adsorption on activated carbon [Data: 12]. As illustrated in the figure, the generalized model can predict the adsorption isotherms about twice the error of the two-parameter OK model.

Several gas adsorption systems were subsequently used to validate this generalized OK model. Figure 10 shows the generalized OK model prediction of our gas adsorption measurements on activated carbon at 318.2 K [13]. A surface area of 920 m^2/g and the solid-solid energy parameter, $\varepsilon^{\bullet}_{CC}/k$, of 39 K, were obtained from the best fit to the CO_2 adsorption data. Using this information and the generalized $C_{a,o}$ and δ, the adsorption isotherms for the other three gases were then *predicted*. A similar prediction procedure was applied for the other systems, confirming that the gas adsorption on activated carbon can be predicted using the generalized OK model with about 7% AAD or about twice the error of the two-parameter OK model.

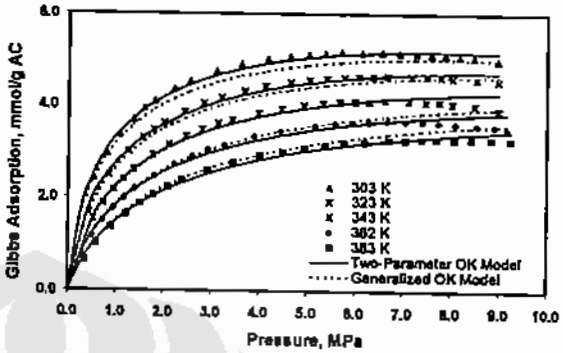

Figure 9.

Comparison of the Generalized Predictions and Two-Parameter OK Model Representations of Methane Adsorption on AC (Data: 12)

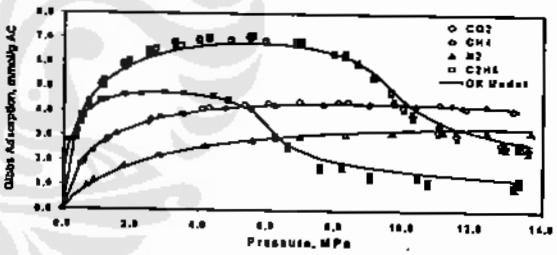

Figure 10.

OK Model Predictions of Gas Adsorption on Calgon AC at 318.2 K

4. Conclusions

The major conclusions of this study are as follows:

- The OK monolayer model appears effective in modeling gas adsorption on carbon matrices at supercritical and near critical region.
- On average, the OK model with two regressed parameters for each system can correlate isotherm adsorptions within expected experimental uncertainties (3.6% AAD).

- The generalized OK model predicts the adsorption on activated carbon with 8% AAD or twice the error of the two-parameter OK model.
- A high potential exist for developing *a priori* predictive model using fully-generalized parameters, that provides reasonably accurate predictions for other gases adsorption isotherms based on adsorption data for one gas at given temperature. This includes the prediction of a maximum in the pure component excess adsorption at high pressures.

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