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Ono–Kondo lattice model for high-pressure adsorption: Pure gases

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ABSTRACT

Theoretical models for adsorption behavior are needed to develop optimal strategies for enhanced coalbed methane (CBM) recovery operations. Although several frameworks are available for describing this adsorption phenomenon, the Ono–Kondo (OK) lattice model offers several practical advantages in modeling supercritical, high-pressure adsorption systems.

In this study, we evaluated the Ono–Kondo (OK) lattice model for correlating high-pressure, supercritical adsorption encountered in CBM recovery and CO_2 sequestration. Specifically, the parameters of the OK model were optimized to obtain reliable representation of pure-gas adsorption on carbon adsorbents. The results were used to develop generalized model parameters, expressed in terms of gas properties and adsorbent characterization which include the temperature dependence of the OK model parameters.

The results indicate that the OK monolayer model appears effective in modeling pure-gas adsorption on carbon matrices. The model can *represent* the adsorption isotherms on activated carbons and coals with about 3.6% average absolute deviation (AAD), which is within the expected experimental uncertainties of the data. The generalized model can *predict* the adsorption isotherms on activated carbon with about 7%AAD. Moreover, generalized model parameters determined from isotherms of a single gas can be used to *predict* the adsorption isotherms of other gases. The generalized model also appears effective for pure-gas adsorption on wet coals when the moisture content in the coal is above the equilibrium value. However, at water contents below the saturation value, the model parameters are dependent on the water saturation.

1. Introduction

To be useful for CBM applications, an adsorption theory should be capable of handling different adsorbate/adsorbent systems over the full range of operating conditions. Among the theories widely used for adsorption modeling are the Langmuir model [1], ideal adsorbed solution (IAS) theory [2], heterogeneous ideal adsorbed solution [3] (HIAS), vacancy solution model [4–6] (VSM), theory of volume filling micropores (TVFM)[7], two-dimensional equations of state models [8–11] (2D-EOS), and the simplified local density (SLD) model [12–15]. In general, these models work well for low-pressure adsorption; however, few are capable of modeling the high-pressure, supercritical adsorption that is of interest in CBM-related work.

In this study, we evaluate the Ono–Kondo (OK) lattice model for correlating high-pressure, supercritical adsorption isotherms encountered in CBM recovery and CO_2 sequestration. In addition to its theoretical origins in lattice theory, the OK model offers several distinct practical advantages. Specifically the model:

1. Describes monolayer and multilayer adsorption.
2. Has the potential to describe adsorption behavior based on the physical properties of the adsorbates and accessible characterization of the adsorbent.
3. Generates direct estimates for the adsorbed-phase densities, which facilitate reliable predictions of absolute gas adsorption.
4. Is structured to incorporate accurate density calculations from equation-of-state models, which reduces the correlative burden on the adsorption model.

The application of the OK model to pure-gas adsorption on activated carbon has been demonstrated by Aranovich and Donohue [16] and Benard and Chahine [17,18]. Recent work on gas adsorption modeling with variants of the Ono–Kondo lattice theory has also been reported in the literature [19,20]. Critical point corrections to the multilayer Ono–Kondo lattice theory have also been formulated [21,22].

The OK modeling results on activated carbons in the literature [16–18] show that the model is in good agreement with experimental data. However, the regressed model parameters from those studies are not entirely suitable for application to other similar systems in the high-pressure, supercritical region. The results also reveal that, although the OK model has the potential to repre-

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sent gas adsorption, the model parameters must be determined with care. This includes (a) determination of the optimal number of layers used to describe the adsorbed phase for a specific system, (b) a general formulation that will produce reasonable estimates for each parameter, and (c) describing the parameters in terms of accessible adsorbate and adsorbent characteristics. These capabilities are important for predicting adsorption of systems beyond those where experimental data are available. Moreover, the temperature dependence of the model parameters must also be evaluated.

In this study, the parameters of the OK model were evaluated to obtain reliable representation (within the expected experimental uncertainties) of pure-gas, high-pressure adsorption on selected carbon adsorbents for adsorbates in the near-critical and supercritical regions. Generalized model parameters were then developed which can predict the adsorption equilibrium to within twice the expected experimental uncertainties.

Extending mathematical models to describe adsorption behavior on coals is complicated by (a) the difficulty in characterizing the coal matrix adequately and (b) assessing the effect of water (found in essentially all coalbeds) on the adsorption behavior. As a result, we decided to perform initial studies (a) on a more readily characterized carbon matrix and (b) in the absence of water (i.e., on dry activated carbons). Our rationale is that useful models should prove capable of fitting data on activated carbons prior to extending them to include the effects of the complex adsorbent structure of coals and/or the presence of water.

To apply the OK model, the number of layers must be specified. Therefore, before performing model parameter evaluations, we determined the number of layers required to best describe the systems considered. The multilayer and monolayer adsorption models were compared, and the more appropriate model was used for the rest of this study. The main sections of the manuscript are organized in the following manner: Section 1 provides a discussion on the main aspects of OK model for pure gas adsorption and the determination of number of layers for the OK model used in this study. Section 2 includes the OK modeling results for adsorption on activated carbon and the basis for model generalization. Finally, Section 3 presents the OK modeling results for pure gas adsorption on dry and wet coals.

1.1. Ono–Kondo lattice model for adsorption

The OK adsorption model is based on lattice theory and was proposed originally by Ono and Kondo [23] and further developed by Donohue and coworkers [16,21,22]. In the lattice model, the fluid system is assumed to be composed of layers of lattice cells that contain fluid molecules and vacancies. For the case of adsorption, more fluid molecules reside in the cells of the adsorbed-phase layers than in the cells of the bulk-phase layers. Molecular interactions are hypothesized to exist only between nearest neighboring molecules. When equilibrium exists between the gas-phase and the multilayer adsorbed phase, the expression for the thermodynamic equilibrium for pure-component adsorption under the mean-field approximation can be written as [16]:

$$\ln\left[\frac{x_t(1-x_b)}{x_b(1-x_t)}\right]+\frac{z_0(x_t-x_b)\varepsilon_{ii}}{kT}+\frac{z_2(x_{t+1}-2x_t+x_{t-1})\varepsilon_{ii}}{kT}=0 \quad (1)$$

for $t = 2, 3, \ldots, m$, number of the layer, and

$$\ln\left[\frac{x_1(1-x_b)}{x_b(1-x_1)}\right]+\frac{(z_1x_1+z_2x_2-z_0x_b)\varepsilon_{ii}}{kT}+\frac{\varepsilon_{is}}{kT}=0 \quad (2)$$

for the 1st adsorbed layer.

In these equations, x_t is the reduced density or fraction of sites occupied by adsorbed molecules in layer t, and x_b is the fraction of sites occupied by fluid molecules in the bulk. For a hexagonal configuration of lattice cells, the coordination numbers z_0 and z_1 are 8 and 6, respectively; and by definition, $z_2 = (z_0 - z_1)/2$. The fluid–fluid interaction energy is expressed by ε_{ii}/kT, and the fluid–solid surface interaction energy is expressed by ε_{is}/kT, where k is Boltzman's constant, and T is the absolute temperature.

The analytical expression for the Gibbs excess adsorption from this model is:

$$\Gamma = C\sum_{t}^{m}(x_t-x_b) \quad (3)$$

where C is a prefactor related to the capacity of the adsorbent for a specific gas, and m is the maximum number of adsorbed layers in an adsorption isotherm. The reduced densities x_t and x_b are expressed as $x_t = \rho_t/\rho_{mc}$ and $x_b = \rho_b/\rho_{mc}$, where ρ_t and ρ_b are the adsorbed and the bulk density of the adsorbate at layer t, respectively, and ρ_{mc} is the adsorbed phase density at maximum capacity.

For simplicity, we have modeled the adsorption as occurring within a slit. For monolayer adsorption inside a slit, the equilibrium expression can be written as [17]:

$$\ln\left[\frac{x_{ads}(1-x_b)}{x_b(1-x_{ads})}\right]+\frac{((z_1+1)x_{ads}-z_0x_b)\varepsilon_{ii}}{kT}+\frac{\varepsilon_{is}}{kT}=0 \quad (4)$$

The Gibbs excess adsorption then simplifies to:

$$\Gamma = 2C(x_{ads}-x_b) = 2C\left(\frac{\rho_{ads}}{\rho_{mc}}-\frac{\rho_b}{\rho_{mc}}\right) \quad (5)$$

1.2. Determination of the appropriate number of layers

As described in the previous section, the OK lattice model can be applied to monolayer or multilayer adsorption. We used selected experimental data to evaluate the number of layers required to represent the systems considered adequately. Specifically, our measurements at 318 K for adsorption of pure nitrogen, methane and CO_2 on activated carbon [24] were used to represent adsorption in the supercritical region; the CO_2 adsorption data on activated carbon measured by Humayun and Tomasko [25] at 304 K were used to represent the adsorption in the near-critical region; and our CO_2 adsorption data on a dry coal (Illinois #6) were used to represent an adsorbent with a wide pore-size distribution [26].

Table 1 presents a summary of our model evaluations for monolayer and three-layer models used to correlate the selected data. The model parameters, given in Table 1, were determined by minimizing the sum of squares of weighted absolute errors in the calculated adsorption, ω, for the pure gas of interest. The weights used in the regressions were the expected experimental uncertainties, determined through multivariate error propagation analysis. In addition, Table 1 presents other measures of the quality of the fits, expressed in terms of absolute average percentage deviation (%AAD) and weighted average absolute errors (WAAE). Figs. 1 and 2 illustrate the quality of representation produced by the models. Both models show excellent representation, within the expected experimental uncertainties; as such, comparable representation is provided by the monolayer and multilayer models. This suggests 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 [17,27,28]. Perhaps, monolayer adsorption is more likely because the size of the micropores is only several times the diameter of the molecules. Since the monolayer model proved effective and adequate in modeling pure-gas adsorption on carbon matrices, it was used in the subsequent calculations reported here.