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Adsorption Equilibrium of Alkanes on a High Surface Area Activated Carbon Prepared from Brazilian Coconut Shells

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Abstract. Adsorption equilibria of methane, ethane, and *n*-butane on a high surface area activated carbon prepared from Brazilian coconut shells is examined in this study. The material shows high capacities for the alkanes tested. A group-contribution theory is used to predict adsorption isotherms for all three components with very good accuracy employing one set of model parameters. The theory is also used to observe trends in isosteric heat of adsorption as a function of loading at various temperatures.

Keywords: adsorption equilibrium, alkanes, nanoporous, group-contribution theory, carbon, coconut shells

Introduction

Activated carbons are commonly used for air and water purification and adsorption of organic vapors. They can be produced from many sources including coal, petroleum residue, wood products, and biomass such as fruit pits and shells. The type of precursor used to synthesize the carbon and the process used for activation determine properties such as surface area and pore size distribution, which greatly affect adsorption properties.

Adsorption equilibria of light alkanes on commercial activated carbons have been reported by several authors (e.g., Do and Do, 1994; Holland et al., 2001; Mangun et al., 1997; Russell and LeVan, 1997), and research and development of materials with high capacities for methane in particular have been spurred by a growing interest in natural gas as a vehicular fuel. The storage and transportation of natural gas is one of the major obstacles facing the commercialization of alternative fuel vehicles due to the low density of methane, and adsorptive storage offers a promising alternative to typical gas storage methods.

A nanoporous material used for natural gas storage and delivery would logically be chosen based on methane capacity and the effect of higher alkanes on a cyclic charge/discharge process. Studies on various types of carbon materials as possible gas storage media have been widely reported (Chang and Talu, 1996; Lozano-Castello et al., 2002; Matranga et al., 1992; Mota et al., 1997), usually focusing on methane adsorption. Recently, an activated carbon obtained from Brazilian coconut shells was evaluated for methane adsorption at pressures up to 40 bar (Cavalcante et al., 2003).

In this paper, we present pure-component adsorption equilibrium data for methane, ethane, and *n*-butane on an activated carbon prepared from Brazilian coconut shells. The data are described by a simple group-contribution theory (Walton et al., 2004), which allows prediction of adsorption equilibrium for components on which no data are available, as well as prediction of mixture adsorption. The proper description and prediction of these data are critical for the design and simulation of a natural gas storage process. Heats of adsorption, which can have a detrimental effect on gas

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storage processes, are also estimated for each component based on the group-contribution theory.

Materials and Experimental Methods

The nanoporous activated carbon was prepared from Brazilian coconut shells by chemical and physical activation in the laboratory of Professor Emerson Jaguaribe (UFPB, Joao Pessoa, Brazil). It has a BET surface area of 2100 m^2/g. Details of the synthesis can be found elsewhere (Cavalcante et al., 2003). Adsorption isotherms for methane, ethane, and n-butane were measured gravimetrically.

Simple Group-Contribution Theory

A persistent problem in any adsorption process involving more than one component is the prediction of mixture adsorption. An accurate description of this behavior while minimizing computation time is especially important for use in gas storage or fixed-bed simulations, where adsorption equilibrium calculations must be repeated thousands of times. The most convenient theories predict mixture adsorption from pure-component data because multi-component adsorption data are difficult to measure, and it is often unreasonable to examine experimentally wide ranges of conditions.

The simple group-contribution theory developed by Walton et al. (2004) based on the work of Russell and LeVan (1996) provides a suitable method for describing and predicting the adsorption of alkanes, both pure-components and mixtures, on nanoporous carbons. The alkane molecules are separated into three groups (CH_4, CH_3, and CH_2) that cover a certain area of the surface. For instance, methane consists of one CH_4 group, and butane is built from two CH_3 groups and two CH_2 groups. So, we have $r_{\text{meth}} = r_{CH_4}$ and $r_{\text{but}} = 2r_{CH_3} + 2r_{CH_2}$.

The theory assumes that the carbon surface can be represented by a hexagonal lattice with patchwise heterogeneity. A local isotherm equation then applies to each patch, and the overall loading is distributed over the surface based on some distribution of energies that is characteristic of the carbon under consideration. The local isotherm equation is given by

$$p_j = \frac{1}{K_j}\frac{\theta_j}{\left(1 - \sum_i r_i\theta_i\right)^{r_j}} \tag{1}$$

where

$$K_j = K_{j0}\exp(\varepsilon_j/kT) \tag{2}$$

$$\varepsilon_j = r_j \sum_\alpha t'_{j\alpha}\eta\varepsilon_\alpha \tag{3}$$

$$\theta_j = n_j/m \tag{4}$$

in which ε_j is the adsorptive potential energy for molecule j, and $t'_{j\alpha}$ is the fraction of molecular elements or groups of a particular type in a molecule. ε_α is the maximum adsorptive potential energy for a particular group, and m is the density of lattice sites.

Because the surface is heterogeneous, the overall loading can be calculated by

$$n_j^{\text{tot}}(P, T) = \int_0^1 n_j(P, T, \eta)\, h(\eta)\, d\eta \tag{5}$$

in which η is a dimensionless adsorptive potential energy given by

$$\eta \equiv \varepsilon_j/\varepsilon_{\max,j} \tag{6}$$

and the dimensionless energy distribution, h, is given by

$$h(\eta) = \frac{\eta^{a-1}(1-\eta)^{b-1}}{B(a, b)} \tag{7}$$

where $B(a, b)$ is the beta function, and a and b are model parameters with values greater than or equal to unity.

The model contains two temperature-dependent parameters, allowing for prediction of adsorption data at various temperatures. K_{j0}, in Eq. (2), is expressed by

$$K_{j0} = k_0\exp(k_1C)/\sqrt{T} \tag{8}$$

where k_0 and k_1 are model parameters and C is the number of carbon atoms in a molecule. For Eq. (3), $\varepsilon_{\max,\alpha}$ is given by

$$\varepsilon_{\max,\alpha} = \varepsilon_{\max,\alpha_0}\left(1 + K_\varepsilon\frac{(T - T_{\text{ref}})}{T_{\text{ref}}}\right) \tag{9}$$

where $\varepsilon_{\max,\alpha_0}$ and K_ε are constants. Using pure-component data, these parameters can be solved for and used to predict adsorption of alkanes for which no experimental data are available because they are based on the interaction of groups (CH_4, CH_3, CH_2) with the carbon surface.

Results and Discussion

Adsorption Equilibrium Data

Pure-component adsorption isotherms are shown in Fig. 1 with the group-contribution theory predictions. From the adsorption measurements, this coconut shell carbon is found to have a remarkably high capacity for *n*-butane, with a loading of roughly 9 mol/kg at room temperature and a pressure of 70 kPa. This characteristic could be attributed to the high surface area of this carbon. It can also be seen from Fig. 1 that this material has a good capacity for methane and ethane as well. The capacities for all three components are better on the coconut carbon than for typical commercially available activated carbons (Walton et al., 2004). In particular, the capacity of butane on this carbon at 298 K and ≈70 kPa is almost 50% greater than the capacity on BAX-1100 carbon (Holland et al., 1999) and more than twice the capacity on BPL carbon (Pigorini, 2000).

The model describes all of the experimental data with very good accuracy as shown by a comparison of calculated and experimental loadings in Fig. 2. It is important to note that one set of model parameters (shown in Table 1) allows the prediction of adsorption data at all temperatures and can be further used to predict mixture adsorption and adsorption of other components such as propane or hexane with no additional model parameters (Walton et al., 2004). This is very convenient for use in gas storage and fixed-bed simulations.

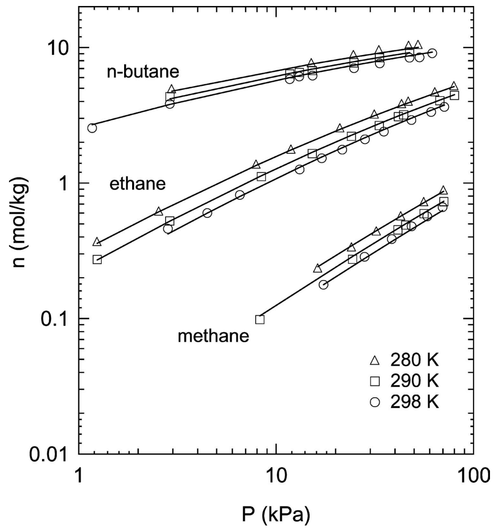

Figure 1. Pure-component isotherms at multiple temperatures on coconut activated carbon. Symbols are experimental data. Solid curves are group-contribution theory predictions (Eq. (2)).

Table 1. Values of parameters in Eq. (1) for adsorption of alkanes on coconut activated carbon.

Parameter	methane	ethane	*n*-butane
K_{j0m} ($\sqrt{\mathrm{K}}$/kPa)	2.308×10^{-5}	4.690×10^{-5}	1.936×10^{-4}
r_j^*	2.9	3.24	5.24
$r_{\mathrm{CH_3}} = 1.62$		$\varepsilon_{\mathrm{max,CH2_0}}/k = 2.399 \times 10^3$ K	
$r_{\mathrm{CH_4}} = 2.9$		$\varepsilon_{\mathrm{max,CH3_0}}/k = 2.752 \times 10^3$ K	
$m = 145.3$ mol/kg		$\varepsilon_{\mathrm{max,CH4_0}}/k = 2.168 \times 10^3$ K	
$a = 5.32$		$K_\varepsilon = -0.0509$ J	
$b = 25.4$		$k_0 = 1.136 \times 10^{-5}$ $\sqrt{\mathrm{K}}$/kPa	
$T_{\mathrm{ref}} = 77.15$ K		$k_1 = 0.709$	

*Calculated from $r_{\mathrm{CH_2}}$ (1.0 by definition), $r_{\mathrm{CH_3}}$, and $r_{\mathrm{CH_4}}$.

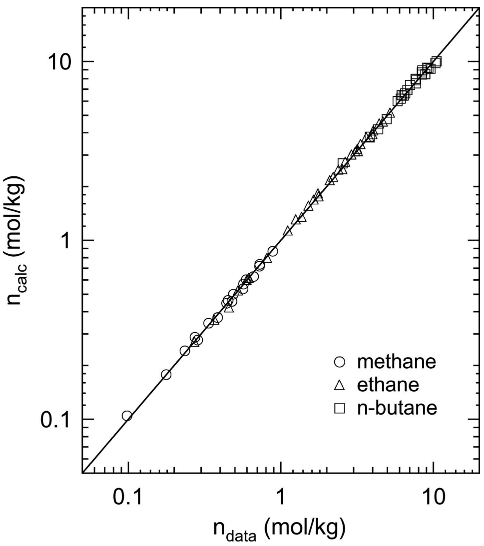

Figure 2. Comparison of calculated loadings with experimental data for methane, ethane, and *n*-butane on coconut activated carbon.

Heats of Adsorption and Heat Capacities

Isosteric heats were examined for methane, ethane, and *n*-butane on the coconut activated carbon using group-contribution theory calculations. The results are shown in Fig. 3. Adsorption heats increase from methane to butane, as would typically be expected. The figure shows that the isosteric heat decreases with increasing loading for all three alkanes. The isosteric heat is also

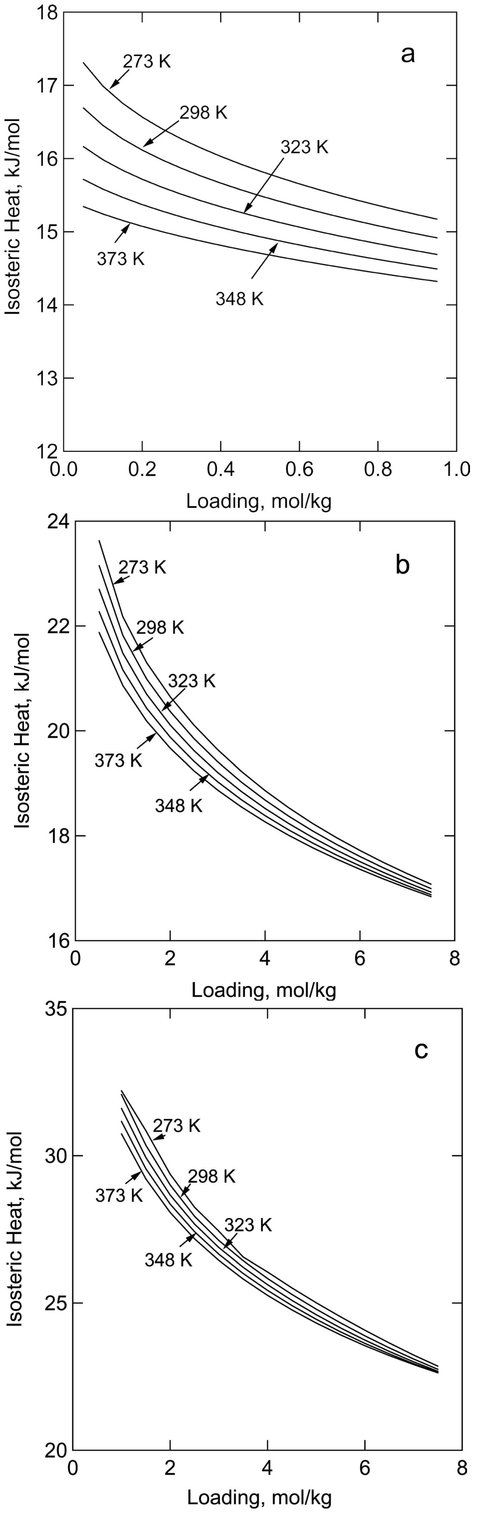

Figure 3. Isosteric heats of adsorption as a function of loading for alkanes at various temperatures calculated from the group-contribution theory. (a) methane, (b) ethane, (c) n-butane.

shown to decrease with increasing temperature; this is similar to vapor-liquid equilibrium for which the latent heat is zero at the critical point.

A thermodynamic analysis shows that a system with a temperature-dependent isosteric heat will have an adsorbed-phase heat capacity that is not equal to the gas-phase heat capacity. Walton and LeVan (2005) showed that the adsorbed-phase heat capacity can vary widely depending on the model used to describe the equilibrium data. Thus, it is important to examine the trends calculated by this model. In Fig. 3, it can be seen that the isosteric heats for the different temperatures approach one another as the loadings increase. This indicates that the difference between the adsorbed-phase heat capacity and gas-phase heat capacity is decreasing with increasing loading. This finding is consistent with a study by Al-Muhtaseb and Ritter (1999) in which the difference between the adsorbed-phase and gas-phase heat capacities was shown to be a decreasing function of surface coverage. Clearly, the group-contribution theory is effective in showing correct trends for isosteric heats for all three components, which is often not true for isotherm models.

Conclusions

The high surface area activated carbon from Brazilian coconut shells has been shown to exhibit high adsorption capacities for methane and ethane and very high capacities for n-butane at room temperature and pressure. The group-contribution theory of Walton et al. (2004) provides a very good prediction of all adsorption isotherms using one set of model parameters. The theory shows well-behaved trends for the isosteric heat of adsorption for each component as a function of loading at various temperatures.

Notation

a, b	parameters of beta distribution
B	beta function
h	single-element dimensionless adsorptive energy distribution function
k	Boltzmann's constant, J/K
K	constant proportional to Henry's constant, kPa^{-1}
m	density of lattice sites, mol/kg
n	amount adsorbed, mol/kg
p	pressure, kPa
r	number of lattice sites covered

$t'_{j\alpha}$	fraction of elements in molecule j of type α
T	temperature, K

Greek Letters

ε	adsorptive potential energy, J
η	dimensionless adsorptive energy
θ	defined as n_j/m, Eq. (4)

Subscripts

α	element index
calc	calculated value
data	experimental value
i, j	component index
max	maximum value

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